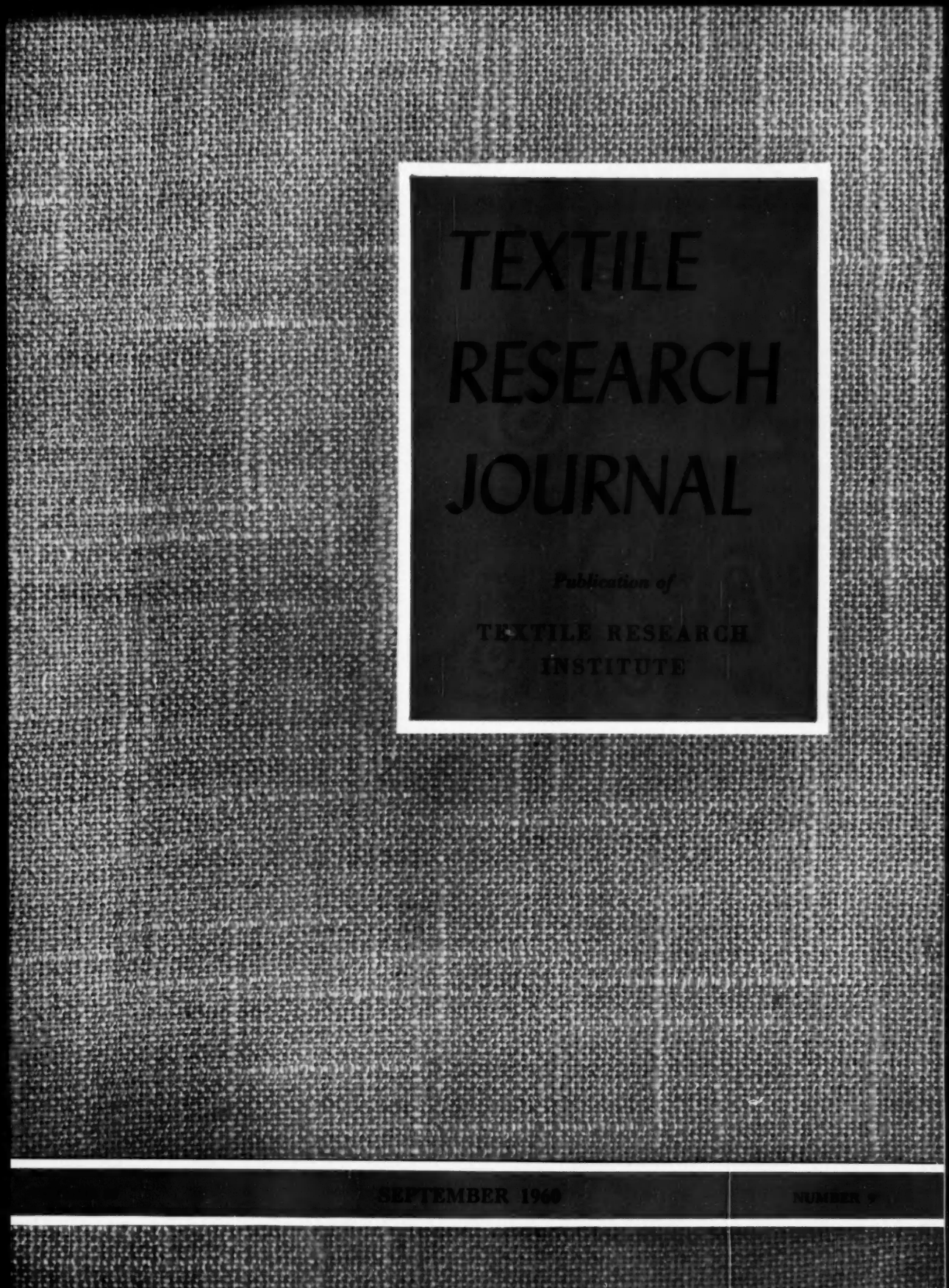
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TEXTILE RESEARCH JOURNAL

Factors Influencing the Cohesion of Worsted Yarns

A. Barella, P. Miró, and R. Crespo

Patronato "Juan de la Cierva" de Investigación Técnica, Sección Textil, Barcelona, Spain

Abstract

In the present paper the different factors influencing the cohesion of worsted yarns, expressed as minimum twist of cohesion, are examined. The study involves (a) the influence of the testing conditions, (b) the influence of fiber parameters, and (c) the influence of the treatments undergone by the fiber.

Introduction

Previously [4, 5, 6, 7] one of the writers had developed the principles of the technique for measuring minimum twist of cohesion and the application of these techniques to the study of the cohesion of worsted and other yarns. These studies led to the establishment of the general properties of the coefficient of minimum twist of cohesion and to the definition of the coefficient of cohesion and its fundamental properties.

However, the necessity for simplifying the measuring techniques, so as to make them practicable for use with conventional apparatus, has led to the establishment of new measuring procedures. The influence exerted by such factors as the test length and the pre-tension applied to the yarn are studied in the present work.

The extension of the studies of minimum twist of cohesion has led to a consideration of the influence exerted on that parameter by fiber characteristics such as length and fineness, as well as by the chemical treatments which the fiber may have undergone. We have examined the possible influence of fiber surface and other factors on the minimum twist of cohesion, relating this parameter to the chemical and structural modifications introduced in the fiber by such treatments.

The parameter defined as "minimum twist of cohesion" or "residual twist" represents the number of turns remaining in the yarn at the moment of its breaking as a result of fiber slippage when the yarn is simultaneously being submitted to an axial pulling and untwisting action. This is a concept similar to Burlet's [8] "drafting twist" and, according to other researchers, a more proper denomination should be sought. Parisot [12] proposes to designate the determination of the new parameter as "maximum untwisting test." During the course of the present work the expressions "minimum twist of cohesion" or "residual twist" will be used without prejudice to the possible later adoption of a more appropriate terminology.

Previous Work

The first experiments were carried out by means of the auxiliary devices of the Barella regularimeter [3]. The measuring technique consisted in fastening the yarn to the stationary clamp of the torsiom-

eter coupled to that apparatus, passing it through the tension measuring device and imparting a convenient previous tension, and then fixing it to the turning clamp of the torsiometer. When untwisting begins, a small drop in tension is first observed on the tension gauge, due to yarn extension; then yarn tension drops sharply as a consequence of yarn breakage through fiber slippage. At this moment the test is stopped and a reading of the twist counter is taken. This is the twist taken out of the yarn within the length limited by the tension gauge and the turning clamp of the torsiometer. Minimum twist of cohesion will be found by subtracting that twist from the original one.

The characteristics of the apparatus used imposed determined conditions on the tests carried out by the above technique, so far as test length (12.5 cm.) and tension are concerned. The latter could not be less than 3 g./tex.

The establishment of a new technique which will later be described showed that the above measuring technique involved a systematic error which tended to underestimate the coefficient of minimum twist of cohesion by about 12.5%; for that reason the technique based upon the use of the regularimeter was replaced by a new one.

However, the original technique allowed a rough study of the principal properties of the minimum twist of cohesion, expressed as a coefficient, in connection with fiber and yarn parameters. The following main conclusions were drawn up:

1. The minimum twist of cohesion does not depend on the applied tension when this lies within a certain range of values.

2. The minimum twist of cohesion is roughly independent of the original yarn twist, when this is not too high.

3. The minimum twist of cohesion depends on mean fiber length. The regression between the coefficient of minimum twist of cohesion τ_t and that length l is a curvilinear one. For worsted yarns, the following expression was obtained:

$$\tau_t = 0.0657\ l^2 - 12.22\ l + 590.56$$

and for cotton

$$\tau_t = 0.13\ l^2 - 8.42\ l + 175.79$$

4. The experimental results do not contradict Hannah's theories contained in her thesis on high draft [10].

5. Taking as a "coefficient of cohesion" the relationship existing between pulling force and normal pressure [14], one may observe that that coefficient is linearly dependent on fiber fineness and that there is a correlation between those two parameters of + 0.867 for worsted and + 0.915 for cotton.

6. The variability of the results obtained in the concerned test is correlated to the twist regularity of the yarn.

Apparatus Used and Testing Technique

At present the authors are using an accurate conventional torsiometer with a simple device to be coupled to the stationary clamp allowing yarn tensioning. Some types of torsiometer are already fitted with such a device.

The testing technique consists in fastening the yarn in the clamps of the torsiometer, submitting

TABLE I

Code	Yarn, metric count	Primitive twist multiplier	Coefficient of minimum twist of cohesion*		Fiber length, mm.	Fineness, μ
			Barella reg.	Torsiometer		
P 1	43	76	36.7	45.0	55.5	21.9
P 2	36	75	38.8	45.2	56.0	21.5
P 3	48	83	44.0	49.0	50.1	19.9
P 4	28	79	45.5	48.0	46.5	20.3
P 5	60	77	39.3	47.2	60.1	20.3
P 6	56	86	41.8	47.5	61.2	20.7
M 1	24	105	32.0	32.8	63.5	24.6
M 2	22	60	32.1	33.8	58.5	23.4
M 3	35	60	33.6	35.0	72.1	23.2
M 4	22	74	27.0	31.0	73.4	31.0
M 5	52	75	28.3	31.7	81.5	25.8

* In Spain the concept of "twist coefficient" is the same as that of "twist multiplier" in U. K. and U. S. A.

the stationary clamp to the predetermined tension. Under these conditions untwisting is started. The testing length becomes progressively extended due to untwisting until a perfectly defined point is reached, at which the yarn suddenly breaks through fiber slippage. The test must be stopped at that moment and the value given by the counter of the torsiometer recorded. This twist has been eliminated from the yarn; therefore, by subtraction of it from the original yarn twist, the residual twist when fiber slippage occurs will be found (the "minimum cohesion twist").

The results may be expressed as minimum twist of cohesion either in turns per meter or as twist coefficient. In this instance the second modality has been used, the coefficient being referred to the inverse metric yarn count system and to turns per meter.

The application of this technique allows carrying out measuring of the minimum twist of cohesion under any conditions of tensioning and test length. The original yarn twist is found, in any case, beforehand, by normal test procedures.

Results

Influence of Pre-Tension and Length of Test Sample

Experiments have been carried out on three worsted yarns under the following conditions:

Tension: 1, 1.5, 2, 3, and 4 g./tex.
Length: 12.5, 25, and 50 cm.

The results are shown in Figures 1–6 and Table I. There is a zone, ranging from 1.5 g./tex to 3 g./tex, in which the coefficient of minimum twist of cohesion is practically independent of the applied tension, remaining almost constant. A rise in the curve from 3 g./tex is observed. This is probably due to the tensions approaching too nearly the fiber tenacity so that it is almost certain that other factors such as fiber breakage were intervening in the experiments.

It follows from Figures 1–3, in which one curve for each test length is shown, that the length of the sample has a definite influence on the results, the coefficient of minimum twist of cohesion varying according to that length. This variation is almost linear, as shown in Figures 4–6, where the coefficient of minimum twist of cohesion has been plotted against sample length. In any case, sample length must always be longer than the longest fiber in order to avoid fibers being gripped at both ends.

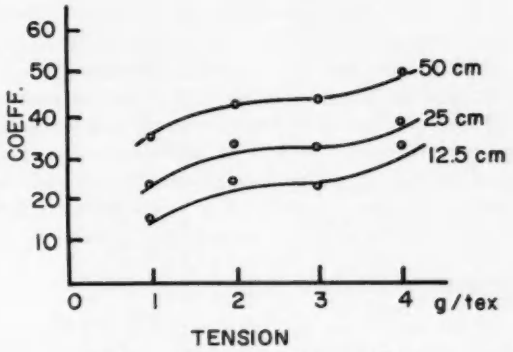

Fig. 1. Yarn count 36 tex (28's).

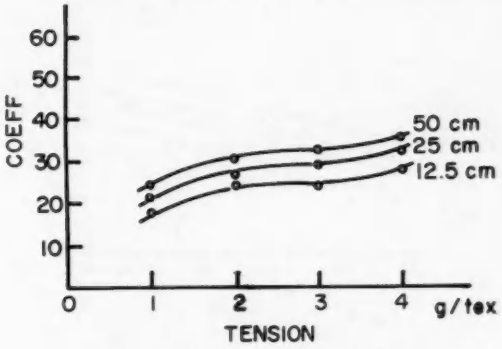

Fig. 2. Yarn count 36 tex (28's).

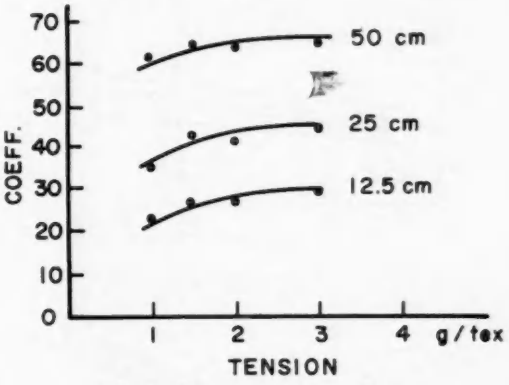

Fig. 3. Yarn count 14 tex (72's).

It follows from these results that there is a need for choosing testing conditions so as to secure the reproducibility of results in further studies. Under these circumstances a tension of 3 g./tex and a length of 12.5 cm. were chosen in order to ap-

proach fiber length as nearly as possible. These conditions correspond to earlier studies [7].

Taking into consideration the characteristics of the analyzed yarns, a tension of 3 g./tex may seem too high. It has been kept so during this series of experiments only because it had previously been used on the old Barella's regularimeter, as well as for comparative purposes. For further tests it will be advisable to decrease tension to 2 g./tex.

Influence of Yarn and Fiber Parameters

It was concluded in a previous work [7] that the coefficient of minimum twist of cohesion found under any given testing conditions depends on fiber length

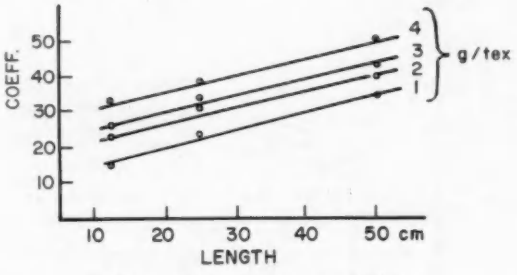

Fig. 4. Yarn count 14 tex (72's).

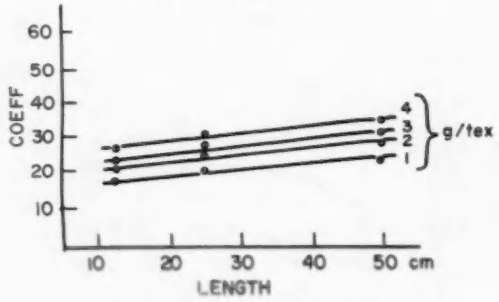

Fig. 5. Yarn count 24 tex (42's).

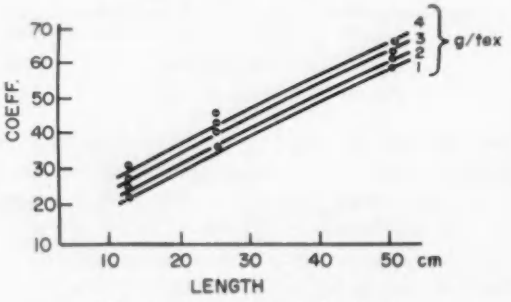

Fig. 6. Yarn count 24 tex (42's).

and fineness and is practically independent of actual yarn twist, so long as the latter does not exceed normal limits (warp twist).

The regression formula found for length as a function of coefficient of minimum twist of cohesion corresponded to limited conditions, since work had been done only on wools the fiber length of which was longer than 60 mm. Besides, the experiments have been carried out on "aged" yarns; i.e., yarns which had been spun long before the cohesion tests took place. All that was known for certain about these yarns was their fiber fineness, but fiber length had also been estimated from a small number of measurements. Moreover, it was realized that there was a possible systematic overestimation of the fiber length, especially for the shorter lengths.

In the present instance, the investigation was carried out on recently spun yarns made from wools of different origins so as to observe whether the relationship between cohesion and fiber parameters could be considered as a general one for wools of a different origin or whether particular properties would be found for each wool quality. For the analyzed yarns, fiber length and fineness had previously been determined by normal procedures (Schlumberger apparatus or three-tweezers method, as modified by Anderson [2], for length and the projection microscope, or "air-flow," for fineness).

Yarns were chosen in such a way that fiber length ranged from 45 to 82 mm. (fiber length al', l') and fiber diameter lay between 18 and 32μ (diameter $MA = (l,d)$). The new technique of the modified torsiometer was applied. Tests were carried out on 11 yarns.

The relationship between the coefficient of minimum twist of cohesion and fiber length and fineness is shown in Figures 7 and 8. It is clear that for yarns of this second series, the fit of the curve is much better for fineness than for length. Moreover, discrepancies among yarns made with wools of different origin are not observed and the fit of the curve is good enough for the different yarns.

The regression between the coefficient of minimum twist of cohesion and fiber fineness may be represented by the following equation:

$$\log \tau_t = 3.7 - 1.54 \log d$$

corresponding to an exponential fitting [19].

Summing up, the influence exerted by the contact surface of fibers acting according to fiber length is

here coming into play. On the other hand, it was also confirmed that there is little dependence between the coefficient of residual twist and the original twist for yarns of normal twist.

The comparison between this series of results and the previous one only necessitates certain modifications in the details of the previous conclusions. These arise from the change and improvement in the measuring techniques and a greater accuracy in fiber length measurements.

Finally, it is worth pointing out here that, from the results obtained in the second series of experiments, it follows that the residual coefficient is more closely related to fiber fineness than to fiber length. This result suggests that the existing correlation with the latter parameter may be a consequence of the separate correlation of length with fineness in wool fibers. However, during the course of the present work other factors intervening in the phenomenon are also investigated.

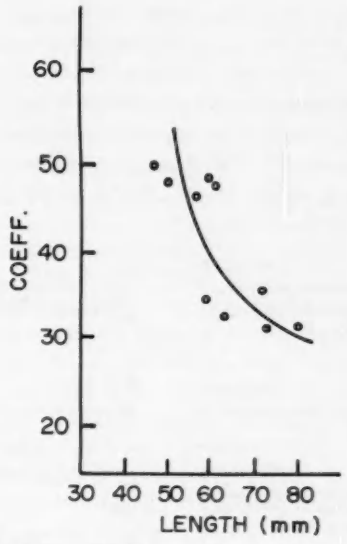

Fig. 7. Coefficient of minimum twist of cohesion vs. length.

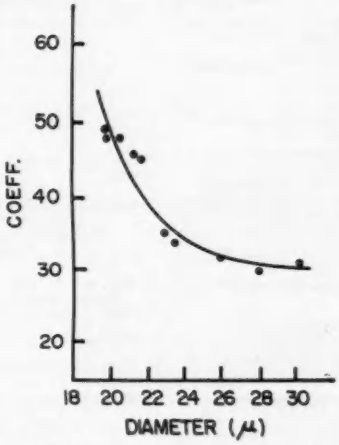

Fig. 8. Coefficient of minimum twist of cohesion vs. diameter.

Influence of Some Chemical Treatments on the Minimum Twist of Cohesion

The above considerations, involving the influence of fiber surface properties on cohesion, also immediately suggest the study of the cohesion of yarns which have undergone particular chemical treatments capable of modifying the fiber surface. Along these lines, the following treatments have been examined.

Treatment A. Samples were treated with a solution of 5 g./l. of sodium carbonate at 40° C. for 10 min. without agitation and then were further washed in distilled water until the rinse water did not show an alkaline reaction.

Treatment B. Samples were treated with a solution of 1 g./l. of Nekanil 0 containing 5 cc. of glacial acetic acid (volume of bath 5 l.) for ½ hr. at 60–70° C., then further washed in distilled water.

Treatment C. Samples were treated with a solution of 5 g./l. of sodium carbonate at 60° C. for 30 min. with agitation, then further rinsed with distilled water until the rinse water did not show an alkaline reaction.

Treatment D. Samples were treated with a solution containing 3% active chlorine on the weight of wool at a pH of 4.5 and with a bath ratio of 1:20. The treatment was cold and lasted for 1 hr., followed by rinsing with water.

Treatment E. The wool samples were immersed in a bath prepared from 100 g./l. of Lyofix A and 40 cc./l. of HCl to 20° Bé. The pH of the bath was 3.6 and the temperature was 35° C. Samples, after soaking, were squeezed between rollers and then dried in an oven at 80° C. for 2 hr. Finally, they were placed in a bath containing 5 cc./l. concentrated ammonia for 1½ hr. at atmospheric temperature; again, they were squeezed between rollers and dried in an oven.

Treatment F. The yarn was impregnated in a mixture made of 5 parts of a spinning oil, 3 parts of Syton W20 (15%) and 8 parts water; then it was squeezed between rollers. The impregnation

and squeezing were repeated. The oil comprised 30 g. of olive oil, 8 g. of sodium oleate, and 56 g. of water. Under these conditions, Syton is applied in a similar manner to the procedure before combing.

Drying was done by exposure to the air.

Treatment G. Yarns were impregnated in a suspension of Syton W20 (15%) in water using a nonionic agent, squeezed, and dried in air. The bath composition was as follows: 15 g. Lissapol N 300, 30 g. of Syton and 65 g. of water.

Treatment H. Samples were twice treated with a solution of 12 g. of fish-glue per liter of water. Then they were squeezed and dried in the air. The bath temperature was 40–50° C.

Treatment I. The same conditions as in the preceding one were followed, but with a greater glue concentration (24 g./l.).

Of these treatments, the first two have been designed so as to eliminate from the wool all traces of oiling present in the yarn. Moreover, Treatment A aims at provoking a slight spontaneous felting of the fiber, while Treatment B is based upon the use of a nonionic detergent.

Treatment C corresponds to the action of an alkaline bath, the conditions being favorable to felting (temperature and bath agitation). Treatments D and E are two nonfelting treatments involving modification of fiber surface. The first one is a chlorination, with the modification brought about on the scales by such a treatment; the second is based upon the coating of the fiber by a product which renders felting difficult (Lyofix A).

Treatments F and G consist of application and coating of the fiber with colloidal silica (Syton), thus also modifying the fiber surface. Finally, treatments H and I consist of a simple sizing by which an increase of fiber adherence is achieved.

The results are shown in Table II as coefficients of minimum twist of cohesion. Fifty tests were made on each yarn before and after treatment.

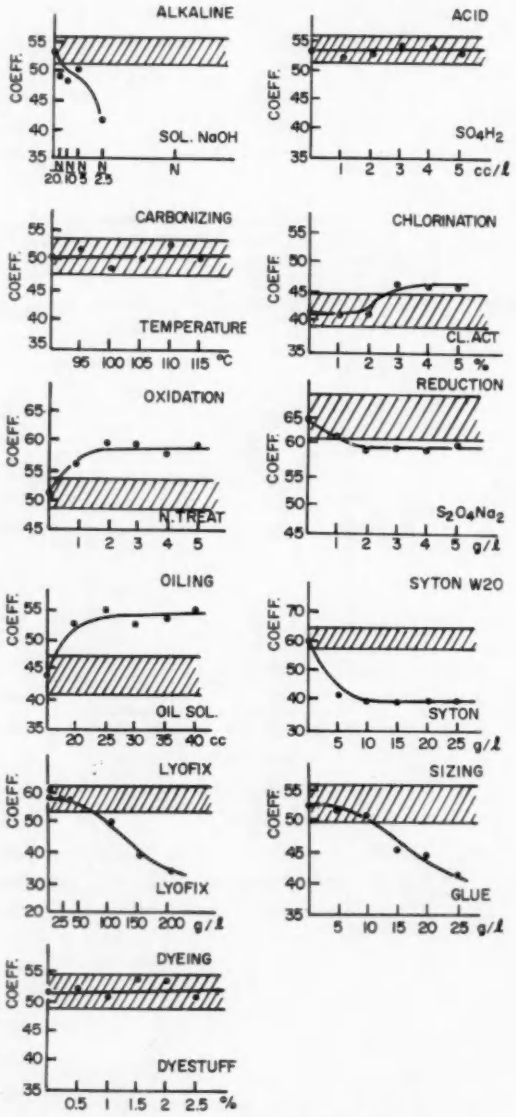

Fig. 9. Effect of treatment on the coefficient of minimum twist of cohesion.

Quantitative Study of the Influence of the Different Treatments on Residual Twist

The consideration of the results corresponding to the different treatments which have been studied seems to show the way to a series of procedures for assessing the effect of a given treatment, whether it belongs to the type of those studied here or not, on the residual twist of the yarn to which it has been applied. Nonfelting treatments, oiling, and sizing, up to a certain extent (with the obvious limitation presented by strong sizing) are particularly appropriate for this kind of test. The main characteristic of all such procedures would be their comparative nature as well as their industrial value, for only a torsiometer fitted with a device to load the sample would be required.

It is also interesting to consider the possible use of this technique as an auxiliary method for detecting fiber alteration. It is well known that there are a certain number of chemical procedures which can be used to detect the chemical alteration produced in the fiber by the action of various treatments. However, there is no equivalent method for physical and mechanical properties since, though many chemical alterations give rise to a decrease in fiber strength, the strength test is not in most cases sufficiently selective. The study of the variations caused by such treatments on the coefficient of residual twist could allow, in certain instances, an identification of the nature of the actual alteration of the fiber.

The procedure, naturally, would be applicable only to yarns, but nevertheless would have interesting possibilities.

In order to study these possibilities, a new series of experiments was carried out so as to reveal, in quantitative form, the modifications introduced in the coefficient of residual twist by different treatments the intensity of which had previously been evaluated. During these experiments, the same experimental conditions have been maintained, except for the length of the sample, which has been increased to 25 cm. in order to avoid simultaneously holding both ends of a fiber when working with wools of different length. Pre-tension of 3 g./tex was used.

Six different types of fiber modification and five other treatments have been examined:

Modification treatments	Other treatments
Alkaline alteration	Oiling
Acid alteration	Lyofix A
Carbonizing alteration	Syton W 20
Chlorination alteration	Sizing
Oxidation	Dyeing
Reduction	

For each of the tested yarns, samples have been taken from the same bobbin and then have been submitted to treatments and modification in five degrees of increasing intensity so as to observe the change in residual twist as a function of that intensity.

Alkaline treatment. Samples have been submitted to the action of increasing concentrations of NaOH solution: $N/20$, $N/10$, $N/5$, $N/2.5$, N.

The treatment was for 1 hr. at atmospheric temperature; bath ratio 1:40.

Acid treatment. Samples have been boiled for 1 hr. in a large bath (1:100) with sulfuric acid (66° Bé) at the following concentrations: 1 cc./l., 2 cc./l., 3 cc./l., 4 cc./l., and 5 cc./l.

Carbonizing. Samples were immersed for 30 min. in a solution of 40 cc. sulfuric acid at 25° C. They were drained to 50% and dried at 80° C, then submitted for 10 min. to the following temperatures: 95° C., 100° C., 105° C., 110° C., and 115° C.

Chlorination. Samples were immersed for 10 min. in a bath containing HCl and Melafix CH. After the samples were wetted out, a sufficient amount of active chlorine, in the form of sodium hypochlorite of 3.23 g./active Cl, was slowly added during 1½ hr. The acidity of the bath was initially adjusted before addition of hypochlorite to pH 2.0.

After chlorination, an antichlor treatment was used in the form of a 3% solution of 40% commercial sodium bisulfite, which was added to the different baths for 10 min.; then a final rinse with distilled water was given.

Bath composition (ratio 1:40)

	1st	2nd	3rd	4th	5th
Water, cc.	75	65	55	45	35
HCl, 1%, cc.	20	20	20	20	20
Melafix 1%, cc.	5	5	10	10	15
Active Cl (% on fiber weight)	1	2	3	4	5

Oxidizing treatment. Samples were treated with hydrogen peroxide at pH 8 (adjusted with sodium metasilicate) and 50° C., liquor ratio 1:40. The solution of hydrogen peroxide as titrated with 0.1 N potassium permanganate was of 1.68 vol. strength.

The treatment consisted in keeping the material immersed in the solution for 1 hr., and was repeated 1–5 times.

Reducing treatment. Samples were submitted for 1 hr. to the action of a range of solutions of sodium hydrosulfite of increasing concentrations, at a temperature of 50° C., in a thermostat, bath ratio 1:50. The concentrations (g./l.) were as follows:

First bath	1
Second bath	2
Third bath	3
Fourth bath	4
Fifth bath	5

Other Treatments

Oiling. An emulsion of 60 g. of olive oil and 16 g. of sodium oleate in 100 cc. of water was first prepared. The following proportions were taken for

the preparation of baths, corresponding to five increasing concentrations:

	Oil, cc. in 40 cc. of water
First bath	20
Second bath	25
Third bath	30
Fourth bath	35
Fifth bath	40

Samples were immersed in their respective baths for 10 min. and then twice squeezed through a pair of rollers. They were then dried in an oven.

Treatment with Syton W20 (Solution to 15%). Bath compositions for the different degrees of treatment were:

	Syton W20, g.	Lissapol N, g.	Water, g.
First bath	5	2.5	52.5
Second bath	10	5.0	35.0
Third bath	15	7.5	27.5
Fourth bath	20	10.0	20.0
Fifth bath	25	12.5	12.5

Samples were then soaked in their respective baths, squeezed between rollers, and dried in air.

Treatment with Lyofix A. The baths contained 40 cc./l. of HCl of 20° Bé and

	Lyofix, g./l.
First bath	25
Second bath	50
Third bath	100
Fourth bath	150
Fifth bath	200

Samples were introduced in their respective baths at a temperature of 35° and pH 3.6. After this, they were twice squeezed between rollers and dried in the oven. They were then washed immediately, immersed in a bath containing 5 cc./l. of concentrated ammonia for ½ hr. at 40° C., then washed, squeezed, and dried again.

Sizing. Baths were prepared from fish-glue in the following proportions:

	g./l.
First bath	5
Second bath	10
Third bath	15
Fourth bath	20
Fifth bath	25

Samples were immersed in their respective baths for 10 min. and then were squeezed between rollers and dried.

Dyeing. Five dyeings were carried out in baths of increasing concentrations of Anthralan Yellow. Bath compositions were as follows:

	Anthralan Yellow, %	Sodium sulfate, %	Sulfuric acid, %
First bath	0.5	15	4
Second bath	1.0	15	4
Third bath	1.5	15	4
Fourth bath	2.0	15	4
Fifth bath	2.5	15	4

The bath ratio was, in each case, 1:50. The material was immersed at 60° C.; the bath was taken to the boil in 1½ hr. and maintained there for a further hour.

Results

The cohesion test was carried out before and after each of the differing degrees of treatment. The results are shown in Figure 9.

The shaded areas in the graphs correspond to non-statistically-significant values.

Discussion and Hypothesis

The study of the data in Figure 9 confirms the influence of the different treatments under test on cohesion as measured by the coefficient of residual twist. Three types of treatments can be distinguished: (a) those increasing the coefficient of residual twist, (b) those not modifying the coefficient of residual twist, (c) those decreasing the coefficient of residual twist. Within each of these groups there are treatments for which the increase or decrease of residual twist is related to the intensity of treatment and other treatments where the influence is neither dependent nor proportional to the intensity with which they have been applied to the fiber.

Treatments increasing the coefficient of residual twist:

- Oiling (from weak concentrations; independent of concentration)
- Chlorination (from 3% of active chlorine; independent of concentration)
- Oxidation (from weak concentration; independent of concentration)

Treatments not modifying the coefficient of residual twist:

- Acid
- Carbonizing
- Dyeing (in acid medium)

TABLE II. Values of the Coefficient of Residual Twist

Yarn	Without treatment			Treatments†								
	$\bar{x}$	Limits ± 2 S.E.		A	B	C	D	E	F	G	H	I
P1	45.0	42.0	48.0	44.8	43.5	44.7	47.3	29.8*	44.3	29.0*	40.6*	23.3*
P2	45.2	43.0	47.7	44.7	41.0	42.5*	47.0	30.5*	40.2	26.4*	37.0*	18.3*
P3	49.0	46.3	51.7	47.6	41.2	46.9	50.0	31.8*	41.8	34.2*	—	—
P4	48.0	45.5	50.5	47.8	47.5	46.0	51.2*	39.5*	46.6	37.8*	42.3*	22.6*
P5	47.2	43.7	51.0	—	45.7	—	53.0*	39.9*	47.0	41.5*	45.3	30.4*
P6	47.5	44.3	50.7	45.1	—	43.7*	49.5	41.0*	41.8*	—	—	—
M1	32.8	27.9	37.7	32.0	30.4	31.5	32.9	24.8	32.5	27.8*	30.6	19.4*
M2	33.8	32.3	35.3	32.8	32.5	31.9*	37.7*	—	27.6*	21.2*	24.5*	20.2*
M3	35.2	32.2	38.2	34.8	34.3	33.0	35.6	27.0*	32.0*	22.4*	25.8*	16.9*
M4	31.0	28.0	34.0	30.6	30.3	29.2	34.3*	21.2*	28.2	22.4*	28.1	22.1*
M5	31.7	27.0	36.4	31.3	—	30.4	38.0*	30.0	31.5	23.8*	28.6	25.7*

* Significant values.

† The scattering of results for treated yarns is roughly of the same order as that of the untreated yarn; for that reason standard errors are not given, as the scattering is less affected by the chemical treatment than by the twist irregularity of the yarn.

Treatments decreasing the coefficient of residual twist:

Alkaline (from weak concentrations; dependent on concentration)

Reduction (from 1.5 g./l. of $S_2O_4Na_2$; independent of concentration)

Lyofix (from 100 g./l.; dependent on concentration)

Syton (from weak concentrations; independent of concentration)

Sizing (from 12 g./l.; dependent on concentration)

Treatments having a significant effect on the coefficient of minimum twist of cohesion fall into two different groups: the first of them includes treatments which modify the fiber surface without affecting the chemical structure of wool; this modification is caused by an addition to the surface of the fiber. The other group includes those treatments which modify the chemical structure of the wool itself, thus causing changes in both the fiber surface and its mechanical properties.

All these treatments modify the frictional coefficient of wool fibers [15] and, consequently, yarn cohesion is bound to be affected. Some of them, such as oiling, chlorination, and hydrogen peroxide treatment, facilitate fiber slippage. Others, such as Syton W20, Lyofix A, alkaline, and reducing treatments, instead make fiber slippage difficult.

Of the treatments which do not produce any chemical modification, oiling increases the coefficient of residual twist; this is quite logical, since the lubricating action of the oil facilitates fiber slippage. On the contrary, sizing as well as treatments with Lyofix A and Syton W20 decreases the coefficient of residual twist, which indicates a greater fiber resistance to slippage. With Syton W20, the silica compound deposited on the surface would increase fiber friction up to a limit, which is quickly reached. This suggests that a greater concentration of the product would merely further deposit on the surface already covered, without changing its character. In the case of sizing and treatment with Lyofix A, spot weldings might be created at the points of contact between the fibers which would prevent fiber slippage. On increasing the concentration of treatment, the number of attachments is increased and so also is the resistance of the fibers to being drawn out. A limiting case may be reached when a compact bulk is formed due to fibers being immersed in either a size or resinous mass.

Treatments causing a chemical alteration of wool also affect, though sometimes in opposite directions, the coefficient of residual twist. The main mechanism of the action seems to be the modification of fiber surface produced by such treatments, but we must not overlook the modification that those treatments also produce on the mechanical properties as a consequence of the chemical attack on the protein molecule. In the case of treatment with *N* sodium hydroxide the attack is so intense that a very perceptible decrease of tensile strength has already taken

place, which precludes the study of the coefficient of minimum twist of cohesion. But even before the attainment of such a profound degradation of the polypeptide chains, modifications of the lateral chains can take place, as well as other changes such as reduction or oxidation of the disulfide link of the cystine, etc., all of them modifying the tensile properties of fibers, and this must necessarily influence the mechanical properties of the yarn and, therefore, the coefficient of minimum twist of cohesion.

In this respect, it is interesting to note the importance that chemical alteration might have on the crimp of wool fibers. It is known from the work of Horio and Kondo [11] that the cortex of that fiber has a bilateral structure and since each part has a different chemical composition, the same reagent produces an unequal chemical attack. For instance, oxidation affects the paracortex more than the orthocortex [16]. According to Leveau, Cèbe, and Parisot [13], the paracortex of oxidized fibers swells more than the orthocortex in chlorine and bromine water. On the other hand, this differential swelling has not been observed for fibers in which the disulfide links have been broken by means of a reducing treatment [16]. On the assumption that the different swelling of the ortho- and paracortex is responsible for fiber crimp [17], it seems likely that such modification of the possible swelling of both parts might affect fiber crimp so far as its mechanical properties are concerned, and together with the surface modifications influence the coefficient of residual twist of yarns.

Of the chemical treatments so far tested, the alkaline and reducing ones, like hydrosulfite, render fiber slippage difficult. Considering the effect of these treatments on the fiber surfaces only, we may base an explanation on the theory of Speakman and Goodings [18] that a superficial dissolution of the fiber by alkali produces a jellylike material which, on drying, would link together the fibers at their points of contact and render their separation difficult. The decrease of residual twist with increasing alkali concentration might be considered as confirmation of such a theory. However, the effect could also be explained in terms of a strong felting, which would involve the destruction of the mechanical properties of the fiber as a consequence of a considerable alteration of the chemical substance.

The small influence of the reducing action exerted by the hydrosulfite seems to suggest that the attack on the disulfide links of cystine has very little importance so long as no simultaneous modification in the mechanical properties and surface structure of the fiber is produced. This view agrees with what has already been said about reduced fibers not showing any anomalous swelling. The small effect on the minimum twist of cohesion may be explained by a slight felting of fibers for, as already known, treatments modifying the cystine link, by replacing it by another one (such as that of the lanthionine, for instance) do not prevent wool from felting.

Oxidizing treatments such as chlorination and treatment with hydrogen peroxide facilitate fiber slippage, and this agrees with the fact that such treatments strongly modify scaliness, as well as with the belief that a rupture of a disulfide link of the cystine produces a nonfelting wool. Because of that surface modification, fiber friction decreases. The curve for hydrogen peroxide is different in its origin from that of chlorination, but this difference may simply be caused by the different intensities of the treatments, since no comparison between the oxidation potential of both solutions has been made at all, quite apart from the fact that other factors might influence the reaction. It is clear that the small concentration of chlorine, in the treatment with Melafix as chlorination auxiliary, does not produce any remarkable modification of fiber surface, this being produced only when concentration is increased; this result is perhaps also influenced by a greater presence of chloride ions [1]. According to what has been said before, the action derived from the composition of the ortho- and paracortex would be superimposed onto this merely superficial one.

The action of chlorine water is, above all, directed to the paracortex, which swells considerably and tends to take on the structure of the orthocortex. The mechanical properties of the fiber are profoundly modified by the disappearance of the disulfide links. In the case of hydrogen peroxide the action is different, since the destruction of the polypeptides chains is less violent.

Conclusions

From the foregoing results, the following conclusions may be drawn.

The new technique for measuring residual twist, employing a modified torsiometer, is more accurate and can with advantage take the place of the one

previously used, based upon the Barella regularimeter.

The initial tension and the length of the test sample affect the results. Consequently, it is necessary to standardize testing conditions.

The study of yarns submitted to different treatment shows the influence of fiber surface on residual twist, which depends on fiber length and fineness as well as on fiber surface.

Chemical treatments capable of modifying either fiber surface or its chemical structure, thus altering its mechanical properties, influence residual twist.

The proposed technique may provide, in certain cases, the basis for a series of test procedures to assess the effect of products and treatments on yarns. These tests, though of a comparative nature, can very easily be applied in industry.

The coefficient of residual twist constitutes both a simple and a practical form, appropriate for industrial applications, of expressing yarn cohesion.

Future Work

The authors intend to carry on their studies on cohesion. In the next phase, work will be carried out on rovings. They also intend to repeat some of the treatments in order to understand better the causes of the phenomenon, using other ranges of concentrations for the products employed. Oiling and Syton treatments will be repeated at lower concentrations.

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Kinetic Study of the Wool-Water System
Part II: The Mechanisms of Two-Stage Absorption

I. C. Watt

C.S.I.R.O. Wool Research Laboratories, Division of Textile Physics, Ryde, N.S.W., Australia

Abstract

The kinetics of the uptake of water vapor by wool is dependent on the initial concentration of water and the size of the concentration increment. For small concentration increments, absorption may occur in two stages, the second stage much slower than the first. For any set of conditions, the previous treatment of the wool with respect to water vapor affects the observed kinetics and the equilibrium concentration of water in the fibers. It is shown that first stage absorption to a quasi-equilibrium obeys Fick's laws of diffusion with a concentration-dependent diffusion coefficient. The apparent activation energy of diffusion varies with concentration. Second-stage absorption is accompanied by irreversible configurational changes within the fibers. Detailed data of two-stage behavior is presented in order to test the relevance to the wool–water system of the hypothesis previously proposed that in polymer–penetrant system second-stage absorption occurs as a result of stress relaxation within the sorbent.

When the sorption behavior of a sorbent–sorbate system cannot be adequately described by any generalized form of Fick's equation of diffusion

$$\frac{dc}{dt} = \frac{d}{dx}\left(D\frac{dc}{dx}\right)$$

where t is the time, c is the concentration at a distance x normal to the sorbent surface, and D is the coefficient of diffusion, the sorption behavior is termed non-Fickian or anomalous. That is, D, the diffusion coefficient, is not constant nor does it bear a direct relationship to the concentration of the diffusing species. Fickian absorption is characterized by an initially linear plot of absorption and desorption as a function of $(\text{time})^{\frac{1}{2}}$. The initial rates of absorption and desorption are identical for a constant value of D, but where D increases with increasing concentration, as is general for polymer-penetrant systems which exhibit Fickian sorption behavior, the initial rate of absorption is greater than the initial rate of desorption.

Polymers in the glassy state, i.e., at temperatures below the second-order transition temperature, usually exhibit non-Fickian sorption behavior with a wide variety of penetrants. Such absorption is frequently characterized by an inflection in the uptake curve as a function of $(\text{time})^{\frac{1}{2}}$, and the initial rate of desorption is faster than the initial rate of absorption.

The cellulose acetate–acetone system has been shown by Mandelkern and Long [13] to behave in this manner for large changes of acetone concentration. If, however, the concentration of acetone at the surface of the cellulose acetate was changed by small amounts, Long, Bagley, and Wilkins [12] found that sorption occurred in two distinct stages. On absorption, the initial uptake to a quasi-equilibrium was rapid and linear against $(\text{time})^{\frac{1}{2}}$ and was followed by a much slower second-stage absorption to the final equilibrium uptake. Similar behavior was observed on desorption.

From kinetic data, Bagley and Long [1] deduced that the first sorption stage was characteristic of Fickian diffusion with a concentration-dependent diffusion coefficient. Absorption or desorption in the second stage could not be fitted by any generalized form of Fick's equation for diffusion. Bagley and Long [1] considered the second stage to be additional absorption or desorption resulting from the slow rearrangement of interchain bonds brought about by the change of penetrant concentration during the first stage.

Similar two-stage sorption behavior has been reported for the cellulose acetate–methylene chloride [1], polystyrene–carbon disulfide, and polystyrene–methylene chloride systems [10] when the polymer was in the glassy state; by Newns [14] for the regenerated cellulose–water system; and by Downes

and Mackay [5] for the wool–water system. It has been shown by Watt [17] that the two-stage behavior observed for a series of interval absorptions in the wool–water system does not occur at 35° C. if the final water concentration in the fibers is below 2.5% or above 20% regain; within this concentration region the form of the absorption curve varies with the initial water concentration within the wool.

In this paper, detailed kinetic data on two-stage absorption is presented and the results are discussed in relation to absorption mechanisms previously proposed for polymer–penetrant systems. It became apparent from the data that the magnitude of the rates of sorption and the equilibrium sorption values vary according to the previous history of the wool sample, although for a standard pretreatment the observed behavior is reproducible and self-consistent. Such behavior is related to internal structure changes as discussed by Barkas [2] for gels in general and by Cassie [3] for wool in particular. It is also probable that the technique of measurement influences the observed sorption behavior. Measurements made in this laboratory on single fibers in air by a vibroscope technique show some differences in detailed sorption behavior which are noted in the text.

Full details of the McBain-Bakr sorption balance, vacuum apparatus, experimental procedure, and materials used in this study have been reported in Part I [17].

Results

Variation of the Size of the Concentration Interval

Sorptions over a small concentration range were termed interval sorptions by Kokes, Long, and Hoard [9] and were carried out in polymer–penetrant systems with concentration-dependent diffusion coefficients in order that the diffusion coefficient would be essentially constant over the concentration range considered. An additional requirement for effective measurement of the separate processes of two-stage interval sorption is that the first stage be completed prior to the commencement of the second stage.

In Figure 1 the increase of regain is shown as a function of $(\text{time})^{\frac{1}{2}}$ when wool samples which had been equilibrated at 47.4% relative humidity and 11.23% regain were exposed to sudden increases of the relative humidity around the fibers. Curve A represents a regain change of 3.4%, reaches equilibrium within 1 hr., and has a shape typical of absorption over a large concentration range, i.e., integral absorption. For a smaller increment of regain of 1.84% (Curve B), the uptake commences quickly but takes 27 hr. to reach equilibrium. Curve D shows an uptake of 1.02% regain. There is a fast initial absorption to a quasi-equilibrium after an uptake of 0.37% regain; the final equilibrium is reached 120 hr. later. It has been found that, for smaller regain increments down to 0.5%, the form of the uptake curve is unaltered; i.e., the relative proportion of uptake in the first and second stages and the times taken to reach the quasi-equilibrium and the final equilibrium are not dependent on the size of the step. Curve E represents a regain change of 0.65%. For regain changes smaller than 0.5%, the accuracy of the experiment makes comparison difficult, but there appears to be little change in the form of the absorption curve.

Curve C represents the absorption curve for a regain change of 1.36%, and although two stages of absorption are clearly evident, it is difficult to decide where the quasi-equilibrium occurs. Therefore, in this work, only regain changes of approximately 1.0% or less have been considered as interval sorptions.

Absorption–Desorption Behavior over Small Concentration Intervals

In has been shown for a number of polymer–penetrant systems where interval absorption occurs in two stages that the uptake of penetrant in the first stage is Fickian. Crank [4] has shown that in Fickian absorption the uptake curves are very similar for the cases of a concentration-dependent diffusion coefficient and a constant diffusion coefficient even over quite large concentration intervals. For the small concentration intervals considered here, the diffusion coefficient can be considered almost constant. For Curves D and E of Figure 1, the uptake in the first stage was compared with the calculated uptake for Fickian diffusion into a cylinder of the same dimensions as the wool fibers. The experimental and calculated curves were in good agreement if the uptake at $(\text{time})^{\frac{1}{2}} = 2.5$ min.$^{\frac{1}{2}}$ was considered as the equilibrium value. The appropriate diffusion coefficient can be calculated and the quasi-equilibrium at the end of the first stage defined as that point past which the uptake can no longer be fitted by a Fickian equation.

If an absorption step carried out under conditions such that two-stage uptake was normally obtained, such as Curve A of Figure 2, was interrupted just as the quasi-equilibrium was reached and the concentration of water vapor reduced to the initial value, it was found that desorption occurred at the same rate as absorption and the regain returned to its initial value (Curve B of Figure 2). On the other hand, if final equilibrium had been established or some second stage uptake had occurred before the water vapor concentration was returned to its initial value, the initial rate of desorption was faster than the initial rate of first-stage absorption, the desorption curve showed a long-term second stage, and the regain of the fibers did not return to its initial value (Curve C of Figure 2). That is, desorption from the quasi-equilibrium showed no hysteresis, but desorption after some second-stage uptake had occurred displayed hysteresis.

Variation of Interval Absorption with Concentration

A wool sample at zero humidity and 35° C. was subjected to small increases of water vapor pressure such that the increase of regain with each step was approximately 1.0%. The wool sample was allowed to come to weight equilibrium after each increment. It has been reported in Part I [17] that, below 2.5% regain, no two-stage behavior was observed and the uptake was Fickian, with a concentration-dependent diffusion coefficient, while above 19% initial regain it was not possible to separate two stages of absorption.

For the regain region from 2.5% to 19%, the proportion of the amount of uptake which occurred in the second stage of absorption varied with the

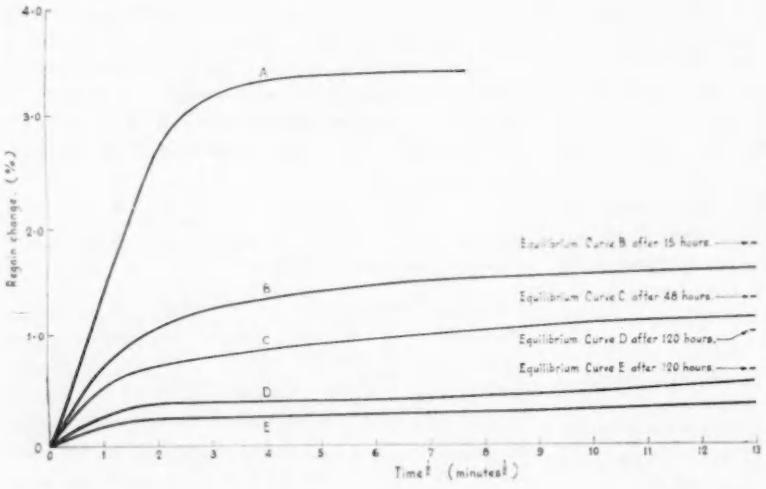

Fig. 1. Regain change vs. (time)$^{\frac{1}{2}}$ for a series of concentration increments from 11.23% regain. Curve A: increment of 3.40% regain; Curve B: increment of 1.84% regain; Curve C: increment of 1.36% regain; Curve D: increment of 1.02% regain; Curve E: increment of 0.65% regain.

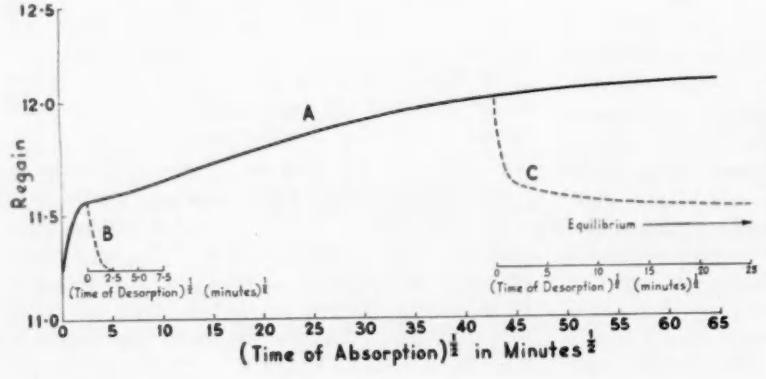

Fig. 2. Interval absorption and desorption at 35° C. Curve A: two-stage absorption following a vapor pressure increment from 47.4% RH to 51.0% RH; Curve B: desorption from the quasi-equilibrium following a return to the initial vapor pressure; Curve C: desorption following a return to the initial vapor pressure after (time)$^{\frac{1}{2}} = 43$ min.$^{\frac{1}{2}}$.

initial regain of the sample. In Table I the final relative humidity of water vapor, the regain range of each absorption interval, the regain at quasi-equilibrium, and the proportion of the uptake which occurred in the second stage for this interval are listed, together with a similar set of results obtained at 50° C.

It is evident that the proportion of uptake in the second stage increases markedly with regain up to 10% regain remains almost constant until 14% regain and thereafter decreases. The behavior at 35° C. and at 50° C. is similar over this concentration region.

The coefficient of diffusion for the first stage of each interval step was calculated, using the appropriate form of Fick's equation for successive sorption intervals and correcting the fiber dimensions for the swelling prior to the commencement of the step. In Figure 3 the diffusion coefficients at 35° C. and 50° C. are plotted against the appropriate values of regain.

The Effect of Temperature

It is evident from Table I and Figure 1 that the largest contributions of the second-stage absorption are observed for regain changes of 1.0% or less in the concentration region of 10–14% regain, i.e., within the approximate relative humidity limits of 42–56% at 35° C. Wool samples were equilibrated with water vapor at 46.4% RH and subjected to a small increase of humidity (3.6% RH) such that the increase of regain was less than 1.0%. After final

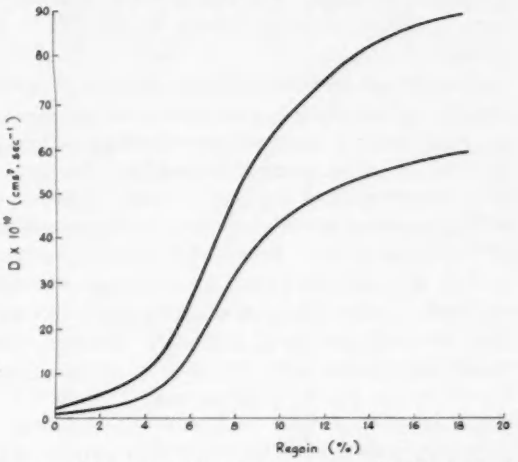

Fig. 3. Diffusion coefficients vs. regain at 35° C. (bottom) and 50° C. (top).

TABLE I

Temperature 35° C.				Temperature 50° C.			
Final relative humidity	Absorption interval as percentage regain	Regain at quasi-equilibrium	Proportion of uptake in second stage	Final relative humidity	Absorption interval as percentage regain	Regain at quasi-equilibrium	Proportion of uptake in second stage
0.76	0 – 0.83	—	—	0.69	0 – 0.78	—	—
1.70	0.83– 1.39	—	—	1.69	0.78– 1.31	—	—
3.20	1.39– 1.90	—	—	2.72	1.31– 1.69	—	—
5.38	1.90– 2.52	—	—	5.51	1.69– 2.37	—	—
9.20	2.52– 3.51	3.45	0.06	7.82	2.37– 3.00	2.97	0.05
13.69	3.51– 4.44	4.29	0.16	12.50	3.00– 3.99	3.89	0.10
17.21	4.44– 5.18	4.97	0.29	17.30	3.99– 4.89	4.67	0.25
20.88	5.18– 5.91	5.59	0.44	21.40	4.89– 5.62	5.38	0.33
26.04	5.91– 6.89	6.37	0.53	25.84	5.62– 6.49	6.11	0.44
30.36	6.89– 7.79	7.30	0.54	30.16	6.49– 7.26	6.83	0.56
35.09	7.79– 8.76	8.13	0.65	34.49	7.26– 8.00	7.58	0.57
39.06	8.76– 9.68	9.10	0.63	39.13	8.00– 8.93	8.34	0.63
42.85	9.68–10.60	9.96	0.70	43.35	8.93– 9.87	9.30	0.61
46.96	10.60–11.59	10.90	0.70	46.96	9.87–10.79	10.18	0.66
50.61	11.59–12.56	11.86	0.72	50.62	10.79–11.72	11.08	0.69
53.42	12.56–13.31	12.78	0.71	53.72	11.72–12.54	11.96	0.71
56.49	13.31–14.24	13.60	0.69	57.43	12.54–13.56	12.84	0.71
59.97	14.24–15.17	14.57	0.65	60.43	13.56–14.41	13.82	0.69
63.47	15.17–16.16	15.55	0.62	63.79	14.41–15.35	14.75	0.64
67.30	16.16–17.16	16.57	0.60	66.74	15.35–16.26	15.69	0.63
70.70	17.16–18.13	17.59	0.56	69.19	16.26–17.06	16.58	0.60
74.34	18.13–19.15	18.64	0.50	72.49	17.06–18.00	17.47	0.56
				76.08	18.00–19.00	18.48	0.52

TABLE II

Temperature, ° C.	Diffusion coefficient D of first stage uptake, cm.²/sec.	Proportion of uptake in second stage	Initial slope of second stage uptake, % regain/min.$^{\frac{1}{2}}$
25.0	5.7×10^{-9}	0.67	0.0057
35.0	7.5×10^{-9}	0.64	0.0067
50.0	10.4×10^{-9}	0.63	0.018
64.7	14.1×10^{-9}	0.65	0.030
77.7	18.4×10^{-9}	0.50	0.047

equilibrium uptake was established, a further relative humidity step sufficient to increase the regain by approximately 1% was made and the weight change of the wool sample carefully followed. The procedure was repeated at five temperatures. The small regain increment occurred in two distinct stages at all five temperatures. It was observed that the first interval step following an integral step attained equilibrium more quickly than subsequent interval steps but that the second and third interval steps reached equilibrium after the same period of time. Therefore the second interval step was used for comparisons at various temperatures. A possible explanation of the variation of the first interval step is that the uptake at a particular relative humidity varies slightly according to the method of reaching the relative humidity value. For example, it was reported in a previous section that wool samples subjected to an integral absorption step of 0–47.4% RH showed an equilibrium uptake of 11.23% regain. The interpolated figures of Table I would indicate an absorption of 11.78% at the same value of relative humidity.

In Table II are listed the temperatures of the absorptions, the diffusion coefficients calculated from the rate of uptake in the first stage of absorption, the relative size of the second stage absorption, and the initial slope of the second stage absorption calculated from the tangent to the absorption curve.

The value of D at 35° C. given in Table II (7.5×10^{-9} cm.²/sec) was obtained for a regain increment of 0.92% from equilibration at 50% RH and 11.88% regain. This value is considerably higher than the value of D in the same regain range at 35° C. to be read from Figure 2 (5.0×10^{-9} cm.²/sec.).[1] The relative proportion of the second stage uptake given in Table II for 35° C. (0.64) is significantly less than the value given in Table I (0.72) for a similar concentration range. The regain after equilibration at 50% RH (11.88% regain) is less than the interpolated value of regain at 50% RH (12.40%) obtained from the figures in Table I. It is apparent therefore that the previous history of a wool sample with respect to water content has an effect on the observed absorption behavior. However, the ratio of the values of D at 35° C. and 50° C. are in agreement for both methods of determination.

The values of the diffusion coefficient of the first stage uptake, D, at the five temperatures are well fitted by an Arrhenius plot

$$D = Ae^{-E/RT}$$

where $R = 1.987$ cal./° A./mole, T is the absolute temperature, A is a constant, and E the Arrhenius parameter representing the energy of activation of the diffusion process. The value of E was found to be 4.6 kcal./mole.

It should be pointed out that this value of E is obtained for absorption from equilibration at a particular relative humidity. However, the regain at a given relative humidity decreases with increasing temperature. Therefore the activation energy measured at a constant regain (say 11.88% regain, which corresponds to 50% RH at 35° C.) will be higher. The variation of diffusion coefficients with regain in this region is not large (see Figure 3), and the estimated difference in the activation energy value by the two methods of calculation is between 0.3 and 0.4 kcal./mole. The value of E at a constant regain of 11.88% would then be 5 kcal./mole.

Analysis of Second-Stage Absorption

It is clear that absorption in the second stage can not be characterized as a simple function of (time)$^{\frac{1}{2}}$. In order to test whether the data followed an exponential relation of the form $y = ae^{bt}$, where y is the uptake at any time t, and a and b are constants, the

[1] A value of $D = 3.5 \times 10^{-8}$ cm.²/sec. at 11.9% regain and 35° C. for the absorption by wool of water vapor in air was obtained in this laboratory [15] by a vibroscope technique.

data was analyzed by a graphical method; log $(A - y)$ was plotted as a function of t, where A is the equilibrium uptake. It was found that for low values of t and high values of $(A - y)$ the curves were convex to the coordinates. However, for small values of $(A - y)$, i.e., as the absorption approached equilibrium, the plots became linear for all curves except for the uptake at 77.7° C. This indicates that the latter part of the second-stage uptake, amounting to 0.25 of the total, can be approximated by a single negative exponential.

An estimate of the energy of activation of the final sorption process was made from the slope of the linear portion of the curves over the temperature range 25°–64.7° C.; it yielded a value of 12 kcal./mole. The initial slope of the second-stage absorption was fitted by an Arrhenius plot; the value of E over the temperature range 25°–77.7° C. was found to be 9 kcal./mole.

Discussion

The First Stage of Sorption

The uptake during the first stage of two-stage absorption in the wool–water system can be predicted by assuming absorption obeying Fick's Laws of diffusion. This suggests that the wool–water system is similar to polymer–penetrant systems, where it has been deduced from kinetic measurements that the mechanism of first-stage diffusion is Fickian. It has been shown in this system that interval absorption and desorption between the initial concentration and quasi-equilibrium occur at the same rate. This fact justifies the assumption that the coefficient of diffusion can be considered as constant over the small intervals of concentration change considered in this work.

The curves of Figure 3 give a measure of the dependence of the diffusion coefficient of the first stage of absorption on the initial concentration of water. This dependence is very small at low regains, but in the regain range of 4–10% it is appreciable, having increased by a factor of 9 at 35° C. Above 17% regain the value of the diffusion coefficient shows only a small increase with regain. However, in this series of experiments, the absorption of water by wool can no longer be termed Fickian if the initial regain is above approximately 19% at 35° C. or 18% at 50° C. Therefore it is not possible to determine whether there is a limiting value of the diffusion coefficient.

An estimation of the activation energy of first-stage diffusion coefficients for absorption from 11.88% regain yields a value of 5 kcal./mole. It has been previously pointed out by Watt [17] that the diffusion of water into wool at low concentrations of water vapor occurs by a Fickian mechanism with a high energy of activation of 11 kcal./mole. The ratios of the values of the diffusion coefficients at 35° C. and 50° C. at a particular regain (Curves A and B of Figure 3) give a measure of the temperature dependence of diffusion on regain. Values at only two temperatures are available for comparison but the ratios observed are consistent with separate temperature-dependence estimations at four temperatures in the range of 35.0–77.7° C. for the regain range of 0–2% and at five temperatures in the range 25.0–77.7° C. at 11.88% regain. The ratio of the diffusion coefficients indicates that the activation energy of the first stage process falls from a value of 11 kcal./mole at zero regain to a value of 5 kcal./mole at 10% regain and remains nearly constant for higher regains.

The value of 5 kcal./mole is in good agreement with the value of 4.8 kcal./mole obtained by King [8] for the activation energy of permeability of keratin membranes at 16% regain and the value of 4.8 kcal./mole obtained by Watt, Kennett, and James [19] for the energy of desorption in the regain range of 10% to 6.5%. It seems therefore that at regains higher than 10% the major mechanism of absorption is no longer attachment of water molecules to high energy sites, as was postulated by Watt [17] for absorption at low concentrations. It is probable that this value represents the energy required for water molecules to overcome the barriers to transport through the fibers and the fibers undergo an elastic expansion without the breaking of interchain bonds.

The Second Stage of Sorption

The second stage of two-stage absorption is generally considered to occur as a result of the breakdown of interchain bonds in glassy type polymers, allowing additional swelling of the polymer and entry of the penetrants. It is difficult to gain direct evidence to support this mechanism. It has been shown by Long and Watt [11] that the second stage of absorption in the cellulose acetate–diacetyl system is not accompanied by steep concentration gradients, thereby indicating that the process controlling ab-

sorption is occurring simultaneously throughout the entire film. This would be expected from a breakdown of bonds as a result of a stress which is evenly distributed throughout the film, as at quasi-equilibrium. Bagley and Long [1] pointed out that the extension–time curves for plasticized cellulose acetate obtained by Haward [7] after the addition of a small load are very similar to the absorption curves obtained after a small step change of penetrant concentration. No such curves have been reported for the decay of stress with time in wool fibers which have been subjected to a small increment of stress.

It has been suggested by Barkas [2] that sorption hysteresis of gels is dependent on the mechanical hysteresis of the gel. From an analysis of the wool–water sorption isotherm Cassie [3] deduced that sorption hysteresis and mechanical hysteresis were related. The fact that no hysteresis is shown on desorption from the quasi-equilibrium but considerable hysteresis is exhibited on desorption after second-stage absorption indicates that mechanical rearrangement of the fibers does not occur during first stage absorption but coincides with second stage absorption.

Evidence of the nature of the absorption in the second stage is given by Curves D and E of Figure 1. Although the magnitude of the concentration range for the absorption represented by these curves is different, the size of the second-stage uptake relative to the first-stage uptake is the same and the form of the curves and the time taken to reach final equilibrium remain the same. If the second-stage absorption occurs as a result of the stress set up in the wool fiber by the first-stage absorption, the initial rate and the size of the second-stage absorption for small regain steps would be closely proportional to the regain increase.

A consequence of this hypothesis which has been pointed out by Newns [14] is that the relative magnitude of the second-stage uptake should increase with increasing initial regain. Newns assumed that at quasi-equilibrium there was a balance between the osmotic forces tending to swell the sorbent further and the elastic forces tending to return the fiber to its original size. The osmotic pressure due to the concentration increment is given by the equation

$$\pi = \frac{RT}{\bar{V}} \times \ln \frac{P_e}{P_q} \qquad (1)$$

where $\bar{V}$ is the partial molar volume of water, P_e the final vapor pressure, and P_q the equilibrium vapor pressure corresponding to the concentration at quasi-equilibrium. For a small concentration change, the elasticity of the wool does not change markedly. There is a volume increment Δv; the cohesive forces restraining the fiber are given by $\gamma \Delta v$, γ being an elasticity coefficient. Newns assumed the cohesive forces to remain constant during the initial stage uptake and obtained the equation for the total amount absorbed relative to the amount absorbed in the first stage to be

$$\frac{M_\infty}{M_q} = 1 + \frac{k\bar{V}}{RT}\frac{\gamma}{\rho} \times \frac{P_q}{\left(1 - \frac{\Delta p'}{2P_q} + \frac{\Delta p'^2}{3P_q^2} \cdots\right)} \qquad (2)$$

where k is the slope of the equilibrium isotherm, ρ is the density of absorbed water, and $\Delta p' = P_e - P_q$.

A guide to the variation of γ in keratin systems is given by the rigidity modulus, as it has been proposed by Feughelman [6] that keratin fibers are not homogeneous with respect to water sorption. He considers that the microfibrils and matrix of keratin fibers can be represented by non-water-absorbing cylinders embedded in a water-absorbing matrix. Thus the absorption of water alters the mechanical properties of the matrix phase only. Consequently the modulus of rigidity, which is independent of the embedded microfibrils, gives a better indication of the behavior of the water-absorbing region than the Young's modulus, which reflects the behavior of the entire fiber. Here we are concerned with the variation of the elasticity coefficient with water concentration, and the quantitative value is not important.

Speakman [16] has published data on the variation of the rigidity modulus with water concentration showing a decrease by a factor of 15 on wetting a dry fiber. By substitution of the variation of the elasticity coefficient, as shown by Speakman's figures, in Equation 2 over the range of humidity from 20% RH to 75% RH and by use of the values of regain given in Table II, it becomes evident that the proportional amount of uptake that occurs in the second stage should increase with humidity at low concentrations and pass through a maximum at approximately 50% RH. The figures of Table I show this to occur. It is apparent, therefore, that the data on the relative size of the second-stage absorption is consistent with the idea of an osmotic balance between the expansion pressure of absorbed water and the cohesive forces of the fiber.

It is clear that the second-stage absorption can not be described as a single exponential process although the latter part approximates to a single negative exponential process. The energy of activation of the initial portion of the second stage uptake at 9 kcal./mole is higher than the energy required for Fickian diffusion through the fibers. It seems probable that there are a number of relaxation processes in the second stage of absorption, the processes have varying time constants, but all have effectively decayed to zero after 0.75 of the second-stage absorption except one high-energy process (12 kcal./mole).

Watt and Kennett [18] have shown that slow configurational changes occur when wool fibers contain water. It is probable that the differences in absorption behavior noted in this paper for interval absorptions at intermediate regains reflect differences in the initial structural configuration of the fibers which have been exposed to a large change of relative humidity as opposed to a series of small humidity changes. Similarly, the changed structural configuration of the fibers permits greater water uptake for a series of interval absorption steps than for an integral absorption step to the same relative humidity.

It may be concluded that two-stage absorption of water by wool occurs for interval absorption at intermediate regains. The proportional size of the second-stage uptake is greatest for absorption from initial regains between 10% and 14%. As the size of the concentration interval is increased above 1% regain, the two stages merge and the typical form of integral absorption is observed.

The uptake during the first stage of absorption occurs by a Fickian mechanism with a concentration-dependent diffusion coefficient. The activation energy of diffusion remains almost constant at 5 kcal./mole above 10% regain, and it is probable that attachment of water molecules to free hydrophilic sites is no longer occurring.

A second mechanism of absorption involving structure changes in the fibers is superimposed on the diffusion mechanism for absorption to a final regain above 2.5%. This mechanism is not a diffusion-controlled action and can not be considered as a single exponential process. The data is consistent with a relaxation mechanism involving the rupture of interchain bonds to allow the decay of the swelling stress caused by the entry of water into the fibers during the first stage of absorption. At high regains the stress relaxation occurs rapidly, following diffusion, so that no two-stage behavior is observed.

The quantitative data obtained from kinetic experiments at intermediate regains is dependent on the initial structural configuration of the fibers, as is also the equilibrium sorption value for a particular relative humidity.

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The Determination of Carboxyl Groups in Cellulose and Oxidized Cellulose

Joseph A. Epstein and Menachem Lewin

Institute for Fibres and Forest Products Research, Ministry of Commerce and Industry, Jerusalem, P.O.B. 8001, Israel

Introduction

The methods available for the determination of carboxyl groups of cellulose and oxidized celluloses are mostly based on the cation exchange capacity of these groups. Accordingly they may be divided into three categories.

1. Methods based on treatment of the sample with a salt solution followed by estimation of the liberated anion; e.g., the cellulose is soaked in a solution of sodium chloride or of calcium acetate and the liberated hydrochloric or acetic acid is estimated.

2. Methods based on treatment of the sample with a salt solution followed by estimation of the cation left in solution; e.g., methylene blue in a solution of methylene blue hydrochloride or silver in a solution of silver ortho-nitrophenolate.

3. Methods based on the direct estimation of the cation adsorbed on the cellulose; e.g., methylene blue adsorbed from a solution of its hydrochloride.

The cation binding by cellulose is an equilibrium process and as such is very sensitive to the conditions under which it is carried out. Factors such as pH or the final concentration of cation in solution may strongly affect the amount of cation absorbed. For this reason methods of Group 3 suffer from the obvious disadvantage that when the excess solution is washed away, some of the bound cation may also be removed, leading to results which are too low.

In methods of Group 1 great difficulties arise from the need to exercise special care in the titration in order to avoid interfering factors such as the presence of carbon dioxide. This will also apply to methods of Group 2 which involve acid–base titrations. While accuracy and reproducibility are the prime considerations in choosing an analytical method, several other factors must also be considered in special cases. Thus, if the method is required for routine analysis of a large number of samples, the simplicity of any method will also be of considerable importance. So long as the shorter time of an analysis does not impair its accuracy to any large extent, preference will be given to the method which best lends itself to routine application. In other cases the amount of material required for a single analysis may be a factor of some importance. This may be so when the determination of carboxyl groups may be just one stage of a wider investigation and where only a limited amount of material is available for this analysis. The present work was carried out in order to determine which is the most suitable method, combining reproducibility and accuracy with relative simplicity.

Experimental

The following methods were tried.

Group 1

1. The calcium acetate method according to Jayme and Neuschaffer [7], which was also employed recently by Uruh and Kenyon [14] and by Sobue and Okubo [13]. The solution of calcium acetate, after standing with the sample, is separated and titrated with $N/100$ NaOH under bubbling nitrogen, with phenolphthalein as indicator. A special tube is used for the titration. The sample is first freed of all cations by washing with dilute acid.

2. The calcium acetate method according to Davidson and Nevell [5]. This method is similar to the above except that the titration is carried out in Nessler tubes and a mixed indicator is used. The color of the solution being titrated is compared with a veronal buffer of pH 8.5 containing the same indicator.

3. Titration method according to Ant-Wuorinen [1]. The sample is first carefully de-ashed with water saturated with carbon dioxide in a special apparatus. The sample is then placed in a closed rocking reactor which holds electrodes, nitrogen inlets and outlets, and reagent inlet and contains about 100 ml. of sodium chloride solution. After equilibrium is reached the solution is electrometrically titrated back to neutrality with $N/100$ or $N/1000$ sodium hydroxide.

4. Titration method according to Meller [9]. This method is similar to Methods 1 and 2 above. The solution, after separation from the sample, is titrated electrometrically to pH 8.3.

Group 2

5. The alkali titration method according to Pacsu [6]. The sample is placed in $N/50$ sodium hydroxide and the residual alkali is titrated with $N/50$ sulfuric acid, with phenolphthalein as indicator.

6. The alkali titration method according to Neale and Stringfellow [11], similar to Method 5. The solution of sodium hydroxide contains sodium chloride and is allowed to stand overnight with the sample. The alkali is then titrated with $N/50$ hydrochloric acid using bromocresol purple indicator and boiling the solution near the end point to expel carbon dioxide.

7. The methylene blue absorption method according to Davidson [4]. The samples are allowed to stand in carefully buffered solutions of methylene blue hydrochloride and the amount of methylene blue left in solution is estimated colorimetrically. An improvement over the original method is the use of silicone coated pipettes for all the volumetric operations involved [10].

8. The silver-*o*-nitrophenol method according to Davidson and Nevell [5]. The samples are placed in a solution containing the above reagent and the amount of silver remaining in solution is estimated by titration with potassium thiocyanate.

Group 3

9. The methylene blue absorption according to Weber [15], also used by Samuelson and Ramsel [12] and tried out by Davidson [4]. The samples are placed in a buffered solution of methylene blue hydrochloride. After standing overnight the samples are removed, washed rapidly with distilled water, and then treated with a large quantity of dilute hydrochloric acid, which removes the dye adsorbed on the cellulose. The amount of dye in the acid solution is then estimated colorimetrically.

Five samples were examined: Israeli cotton (Acala variety) and American cotton (Deltapine variety). These were purified by a method similar to the one described by Conrad [3], which consisted of extraction with boiling alcohol followed by four treatments with boiling 1% sodium hydroxide for 2 hr. each. Between the alkali boils the cottons were boiled for 15 min. with distilled water. After the final alkali boil, a further treatment with boiling water was given, followed by several washings with cold distilled water, a wash with dilute acetic acid, and further washings with distilled water until the washings had the same conductivity as the original water. Purified and bleached cotton linters were a product of Hercules Powder Co. Two samples of oxidized celluloses, designated OX1 and OX2, were prepared by treating the cotton linters with sodium hypobromite at pH 9; this treatment produces mainly carboxyl groups [2]. The hypobromite was prepared by adding an equivalent amount of potassium bromide to a solution of sodium hypochlorite [8]. The oxygen consumptions were 17.8 mg. atoms/100 g. for OX1 and 5.0 mg. atoms/100 g. for OX2.

Results and Discussion

The results are given in Tables I and II. Table I gives some of the individual results of some of the determinations, showing the reproducibility of the results. The number of determinations in each case is not sufficient for a statistical analysis to be made; all the same, the figures give an indication of the reproducibility which was found in the different methods. An approximate indication of the reproducibility is given in the last column but one of this table, which gives the difference between the highest and lowest value obtained. A glance at this column shows that Methods 5 and 9 show poor reproducibility; Methods 1, 2, 4, and 6 show medium reproducibility; while Methods 3, 7, and 8 show good reproducibility. These results are significant in that they indicate that methods which depend on acid–base titrations can achieve reproducibility only when elaborate precautions are taken (Method 3), whereas methods based on a different system may achieve the same degree of reproducibility with a simple procedure (Methods 7 and 8). The reasons for the poor reproducibility of Method 9 have already been indicated. Indeed, it is difficult to see how any method of the Group 3 type may attain a reasonable amount of accuracy.

Table II gives the individual results obtained by each method. These results are averages of 2–6 determinations in each case. Of the methods which show good reproducibility, Methods 7 and 8 show good agreement between themselves. This is not surprising, since these methods are of the same group. The lower results of Method 3 are, however,

TABLE I. Reproducibility of Results in Methods for Determining Carboxyl Groups in Cellulose

Method	Sample	Run I	II	III	IV	V	VI	Δ Max	Reproducibility
1	OX1	6.30	6.46	6.80				0.50	Medium
	OX2	2.47	2.44	2.48				.04	
2	OX1	6.56	6.36					.20	Medium
	OX2	2.27	2.33	1.93				.40	
3	OX1	4.48	4.44					.04	Good
	OX2	1.17	1.19					.02	
	Deltapine	0.16	0.10					.06	
4	OX1	7.60	7.68					.08	Medium
	OX2	1.92	2.04					.12	
	Linters	0.06	0.07					.01	
5	OX1	7.82	8.98	8.89	6.52	7.20	6.55	2.46	Poor
	OX2	2.77	2.78	2.88	2.27	2.58	1.92	.96	
6	OX1	(6.28)	5.65	5.56	5.42			.23	Medium
	OX2	1.38	1.53					.15	
	Linters	0.10	0.18					.08	
7	OX1	5.91	5.86					.05	Good
	OX2	1.68	1.63	1.62				.06	
	Linters	0.89	0.86	0.85				.04	
8	OX1	5.60	5.62	(5.48)	5.62			.02	Good
	OX2	1.95	1.95					.00	
	Linters	0.58	0.35					.23	
9	OX1	4.63	4.89	5.19	4.34			.85	Poor

TABLE II. Results of Carboxyl Group Determinations

Sample	1	2	3	4	5	6	7	8	9
Deltapine	—		0.13	—	—	—	0.50	0.62	—
Acala	1.50	0.85		0.06	—	—	0.33	0.36	—
Linters	2.40	0.89	0.59	—	—	0.14	0.87	0.47	—
OX2	2.46	2.30	1.18	1.98	2.45	1.46	1.64	1.95	—
OX1	6.52	6.46	4.46	7.64	6.52	5.73	5.89	5.58	4.76

TABLE III. Comparison of Methods for Determining Carboxyl Groups in Cellulose

No.	Method	Author	Washing	Analysis	Duration of contact	Duration of analysis	Quantity of sample, g. Max.	Min.	Reproducibility	Special apparatus
1	Calcium acetate	Jayme and Neuschaffer	Dilute HCl	Acid–base titration	Overnight	10 min.	1	1	Medium	Simple titration tube
2	Calcium acetate	Davidson and Nevell	Dilute HCl	Acid–base titration	Overnight	10–20 min.	1	1	Medium	Nessler tubes
3	Sodium chloride	Ant-Wuorinen	CO_2 water	pH titration	Several hours	Several hours	2.5	1	Good	Automatic titration reactor etc.
4	Calcium acetate	Meller	0.1 *N* HCl	pH titration	Overnight	10 min.	1	1	Medium	Setup for pH titration
5	Alkali titration	Pacsu	1–2% H_2SO_4	Acid–base titration	3–5 min.	10 min.	1	1	Poor	Nil
6	Alkali titration	Neale and Stringfellow	1–2% H_2SO_4	Acid–base titration	Overnight	20 min.	1	1	Medium	Nil
7	Methylene blue	Davidson	Not necessary	Colorimetric	Overnight	30 min.	0.50	0.07	Good	Colorimeter
8	Ag-*o*-nitrophenol	Davidson and Nevell	Dilute HCl	Volhard titration	Overnight	30 min.	5	0.5	Good	Nil
9	Methylene blue	Weber	Not necessary	Colorimetric	Overnight	30 min.	1	1	Poor	Colorimeter

disturbing. A possible explanation may be that the de-ashing procedure was not thorough enough. Of the other methods, 1, 2, and 5 show good agreement with each other, whereas those of Method 6 are lower and those of Method 4 are low in one case (OX2) and higher in another (OX1). These remarks refer to the oxidized samples. For the non-oxidized samples the disagreement among the various methods is considerable. The only two methods which agree with one another are Methods 7 and 8, whereas Method 3 gives a similar result for linters but a low one for cotton.

Summarizing, it may be concluded that, for measurements requiring reproducible results, Methods 3, 7, and 8 are suitable. Methods 1, 2, 4, and 6 are suitable for work involving celluloses of carboxyl content higher than about 2 mmol./100 g., whereas Methods 5 and 9 seem to be not sufficiently reproducible.

As indicated above, other considerations apart from reproducibility may also have to be taken into account. From the point of view of the time taken for an analysis, Method 5 has the advantage. This of course explains the poor reproducibility obtained with this method, since in such a short time the reagent may be assumed not to penetrate all the phases of the fibers. Method 3 is the longest, while all other methods require overnight soaking followed by a quick separation and analysis.

The amount of material required for analysis is also an important factor. Methods 1, 2, 4, 5, 6, and 9 prescribe 1 g. for a determination, irrespective of the number of carboxyl groups in the sample. This explains the poor results obtained in most of these methods when samples of low carboxyl content were analyzed. Method 3 prescribes 1–2.5 g. of material according to the number of carboxyl groups. Method 8 prescribes 0.5–5 g. of sample. Method 7 is the most advantageous from this respect, requiring only 0.50 g. for samples of very low carboxyl group content and 0.07 g. for samples of carboxyl content in the range of 8 mmol./100 g.

A still further consideration is the simplicity of the apparatus required for an analysis. Methods 1, 2, 5, 6, and 8 require no special equipment other than the usual volumetric glassware. The special titration tube of Method 1 is very simple to construct. Method 3 requires an elaborate setup containing automatic pH titrator, conductivity bridge, and a rocking reactor. Method 4 requires a pH titration setup and Method 7 and 9 require a suitable colorimeter.

In conclusion, it may be said that Method 3 is suitable for accurate and reproducible work where the amount of material and the time required for an analysis are of secondary importance only. Method 8 is suitable for accurate work where the amount of material available is not limited but where the facilities for expensive setup are not available. Where a suitable colorimeter is available, Method 7 may be recommended for accurate work. It is also suitable for routine work and for work where the amount of material available is limited. Methods 1, 2, 4, and 6 are suitable for routine work but for samples of low carboxyl content larger quantities of material should be taken. The reproducibility of the results in these methods depends on the care exercised in the manipulation. Method 9 seems to be unsuitable for any kind of work, whereas Method 5 may be employed in cases where a quick indication of the order of the carboxyl group content is required.

The various points discussed above are summarized in Table III.

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Relationship Between Fiber Properties and Fabric Wrinkle Recovery[1]

W. W. Daniels

Dacron[2] Research Laboratory, E. I. du Pont de Nemours and Co., Inc., Kinston, North Carolina

Abstract

This research was undertaken to obtain a better understanding of the role of fiber properties in determining fabric wrinkle recovery. For a variety of fibers a one-to-one correspondence was found between fabric crease-angle recovery and a modified tensile recovery parameter, i.e., the average value of tensile recovery (over the range of strains imposed during creasing) measured against a restraining force related to the coefficient of interfiber friction. From this index of recovery, it was predicted that fabric bending recovery would tend toward zero with decreasing strain (increasing radius of crease curvature). Such behavior was observed in the fabrics of nylon and Dacron[2] polyester fiber subsequently studied. The tensile recoveries under load, effective frictional restraints, and qualitative fabric-recovery features are presented. The results reported here indicate that the predominant fiber properties controlling fabric recovery can be determined without recourse to a complete mathematical treatment. Consideration of a simple, idealized model showed interfiber friction to be a property which must be considered in order to obtain even a qualitative description of the mechanism of fabric recovery from deformations involving small strains.

Introduction

The mechanics of bending assemblies of fibers has been the subject of many theoretical studies. Proceeding from simple fiber bending, successive refinements have been introduced to include the effects of twist and packing on bending strain [2, 3, 4, 6, 7, 10]. A complete description of such a system would necessarily include interactions of adjacent fibers. In view of the complexity of an exact treatment, an attempt was made to obtain a qualitative understanding of the effects of interfiber friction on fiber recovery in a semi-empirical way. Specifically, it was sought to relate isolated fiber recovery and interfiber friction to fabric recovery from controlled creasing conditions.

Experimental

Materials

For this work, a series of plain-weave fabrics of roughly comparable construction made from low-twist continuous-filament yarns was selected. Although it would have been desirable to use yarns stripped from the test fabrics for tensile measurements to insure equivalence of previous history, the presence of weave crimp and consequent uncertainty in interpreting the stress–strain curves made this unfeasable. Therefore, all tensile tests were performed on yarns similar to those used in the preparation of the test fabrics after finishing treatments similar to those given the fabrics, i.e., scouring, heat setting (for the thermoplastic items), and a final relaxed boil-off before conditioning in a constant-humidity room.

Fabric-Recovery Measurement

Wrinkle recoveries were measured on conditioned fabrics following the procedure outlined for this test [1] except for variations in the creasing weight and time intervals as indicated below. Swatches were held creased with a 1.5-lb. weight for a period of 2 min., after which they were removed and allowed to recover for 2 min. Two minutes' holding and recovery times were chosen to correspond to the respective cycles in tensile testing as described below. Some of the samples were tested wet at 60° C. to extend the range of recoveries to lower values. For these samples, presoaking was followed by creasing as described above but with samples immersed in

[1] Presented at a meeting of The Fiber Society, Inc., New Orleans, March 10, 1960.

[2] Trademark for Du Pont's polyester fiber.

a constant-temperature bath. After being creased, they were removed from the water bath for recovery in air at room temperature.

Tensile Tests

Tensile tests were performed on the Instron, using a 10-in. sample length and a 10%/min. extension rate. Extension and recovery cycles are shown in Figure 1. Samples were extended to the desired elongation, OA, and held at constant length for 2 min. At the end of this period, the cross-head was returned to the original gauge length (for free recoveries) and the fibers allowed to recover for 2 min. Finally, the samples were re-extended and the unrecovered length BC measured. The tensile recovery was given by

$$\%TR = \frac{OA - BC}{OA} \times 100$$

Fresh samples were used for successive measurements to obtain curves covering a range of initial extensions. For recoveries against a restraining load, the same procedure was used up to the end of the stress-decay period. At this point, the cross-head was raised until the load fell to a predetermined level of restraint. The samples then were allowed to recover length at constant load. After the 2-min. recovery period, the cross-head was returned to the starting position to obtain the unrecovered length BC.

To obtain the data for Dacron and Orlon [3] under 60° C. wet conditions, samples were extended in a thermostatted water bath attached to the Instron cross-head and held at constant length in water for the 2-min. stress-decay period. After stress decay, the water bath was lowered from the sample and recovery was allowed to take place in air.

Friction Measurements

Various methods are described in the literature for determining the coefficient of fiber-on-fiber friction [5, 8, 9]. In these studies, the dependence of the observed coefficient on fiber finish, fiber diameter, normal pressure, speed, and the geometry of the system is pointed out. Since the coefficients of friction desired here were those of the yarns as they existed, with respect to finish and denier, in the test fabrics, the following procedure was used.

[3] Trademark for Du Pont's acrylic fiber.

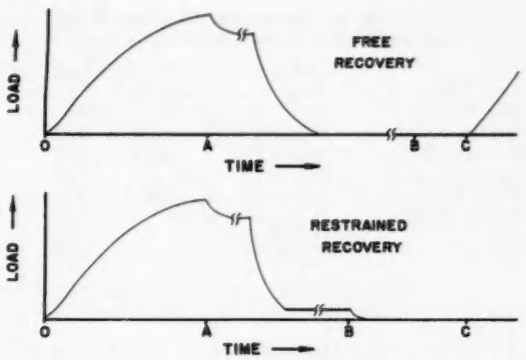

Fig. 1. Load-versus-time cycles for measurement of tensile recovery. Upper curve—free recovery; lower curve—restrained recovery.

Yarns were stripped from the fabrics and wrapped around a ½-in. diameter mandrel. In wrapping the mandrel, care was exercised to insure essentially parallel yarn wraps at right angles to the axis of the mandrel. The mandrel was attached to the upper (strain gauge) clamp on the Instron tensile tester. A length of yarn with a 10-g. weight attached to one end was passed 180° around the mandrel parallel to the wrapped yarns and attached to the lower (cross-head) clamp at the other end. The cross-head was lowered at 0.2 in./min. and the maximum loads before slipping recorded. After several stick-slip readings were observed, the yarn was shifted to another position on the mandrel and the process repeated until 150–200 readings were obtained. The average of these readings (minus the 10-g. input weight, which was also supported by the strain gauge) was used as T_2 in computing static coefficients of friction, μ, from the belt-friction formula,

$$\frac{T_2}{T_1} = e^{\alpha\mu}$$

where in this case $T_1 = 10$ g. and $\alpha = \pi$.

Fabric construction and wrinkle-recovery data are given in Table I along with fiber-on-fiber coefficients of friction.

Treatment of Data

Correspondence Between Tensile and Bending Recoveries

Since an exact analysis of the creasing and recovery processes was beyond the scope of this work, a greatly simplified model was considered in which it was assumed that the only strains existing were

TABLE I. Fabric Construction, Monsanto Wrinkle Recovery, and Fiber-on-Fiber Friction Data

Sample	Construction, warp × fill	% Recovery*	μ†
Dacron, T-56	152 × 100	86 (45)	0.40 (0.42)
Dacron, T-62‡	148 × 102	83	0.42
Experimental fiber	152 × 100	65	0.46
Orlon, T-81	140 × 92	65 (30)	0.54 (0.52)
Nylon, T-200	122 × 108	74	0.45
Silk	120 × 88	74	0.56
Acetate	140 × 72	51	0.61

* Values in parentheses were obtained from samples creased in 60° C. water, removed after 2 min., and allowed to recover in 21° C. air.

† Parallel fiber-on-fiber coefficient of friction. Values in parentheses from samples measured wet.

‡ Specially prepared sample with round cross section.

TABLE II. Yarn Break Elongation vs. Filament Damage in Crease

Yarn elongation, %	Broken filaments in crease
5.0	None
2.9	2–3
1.5	All

tension and compression in the bend and that the strains in all bent fibers were essentially equivalent. From the data given by Hamburger et al. [6], the maximum strain levels at the outside and inside of the bent fibers were found to be approximately 3%. In addition, an experimental estimate of the maximum strain was made. Fabric strips of Dacron were treated in sulfuric acid at the boil so as to embrittle the fibers by decreasing the molecular weight without reducing the diameter. Yarns were stripped from these fabrics and their break elongations measured. The strips were then creased in the usual manner and the creased regions examined for broken filaments. The results are listed in Table II. The onset of broken filaments in the neighborhood of 3% yarn break elongation is in good agreement with the calculated value.

For the low level of strain involved in creasing the test fabrics, it was also assumed that the neutral axis in bending lay in the center of the fiber, that the stress–strain curves in tension and compression were identical out to 3% strain, and that recoveries from both types of strain were equivalent. Under these assumptions, the bending recovery of an isolated fiber can be approximated by averaging the tensile recoveries from zero, the neutral axis, out to 3%, the maximum strain.

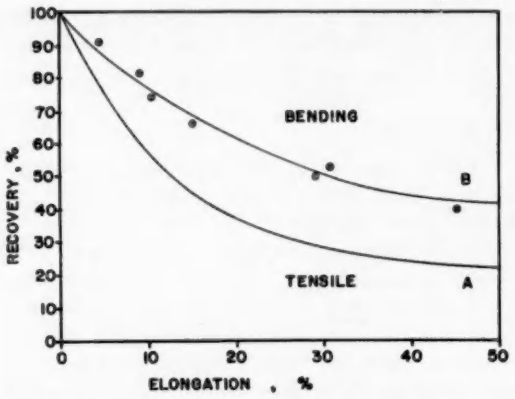

Fig. 2. Recovery versus maximum strain for Mylar polyester film. Tensile recoveries are given by Curve A. Film bending recoveries are given by the points about Curve B.

In this connection, an experiment performed by D. E. Bosley of this laboratory is of interest. Mylar[4] polyester film was bent 180° over spacers of varying radii using a procedure similar to that used in the Monsanto wrinkle-recovery test. The tensile recovery-versus-strain curve was obtained for the same film. In Figure 2, the tensile recovery behavior is shown in Curve A. Curve B represents the calculated bending recovery curve computed from A. The recovery from a bending deformation in which the maximum strain is E is given by the average value of the tensile recovery Curve A from zero to E. The fit of the observed film-bending recoveries, shown by the open circles, to the calculated curve at lower levels of strain is not surprising. However, at higher strains, in which buckling must have occurred, the correspondence was unexpected. The points shown in Figure 2 could have been calculated from any of a variety of neutral-axis locations and corresponding assumptions as to the ratio of tensile to compression recovery; consequently this experiment does not necessarily confirm the validity of the assumptions made. However, similar results to be described below obtained using fabrics indicate that, provided residual strains are diminished by a relaxation treatment, a correspondence between bending and tensile recoveries exists.

Interaction of Recovery and Friction

Tensile-recovery curves, free and at two levels of restraint, are shown in Figure 3 for T-62 Dacron and

[4] Trademark for Du Pont's polyester film.

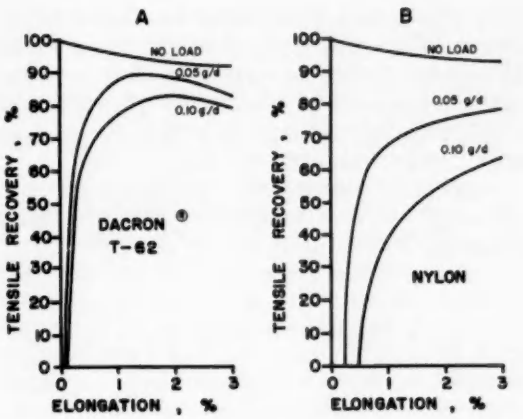

Fig. 3. Tensile recovery-versus-strain curves for T-62 Dacron and nylon at various levels of restraint.

nylon. The features of these curves are of particular interest. That the recovery against a restraint should approach zero for small strains is apparent when it is considered that for a deformation which just exceeds the restraint, no force is available for recovery. Some recovery is possible if the stress exceeds the restraint after stress decay. Percentage recovery against the restraint will increase as the strain is increased, but can never exceed the free recovery.

The average value of each of these curves was determined by integration from zero to 3% strain. The curves shown in Figure 4 depict the behavior of the average restrained tensile recovery as a function of restraining load. If the effective restraint acting on the fibers in a given fabric were known, and provided the assumptions given above were approximately correct, the fabric bending recovery could be estimated from the average tensile recovery under that restraining load. Since, however, the coefficients of friction rather than the actual frictional forces were known, the data in Figure 4 and Table I were examined to determine whether or not a relationship existed between the coefficients of friction and the restraining loads at which the average tensile recoveries were numerically equal to the fabric recoveries. A relationship was found and is shown in Figure 5. Here, the logarithms of the restraining loads for equal average-tensile and fabric-bending recoveries are plotted against the coefficients of friction. If this line is used to determine "effective" restraining loads from measured values of μ, the correlation between average recovery

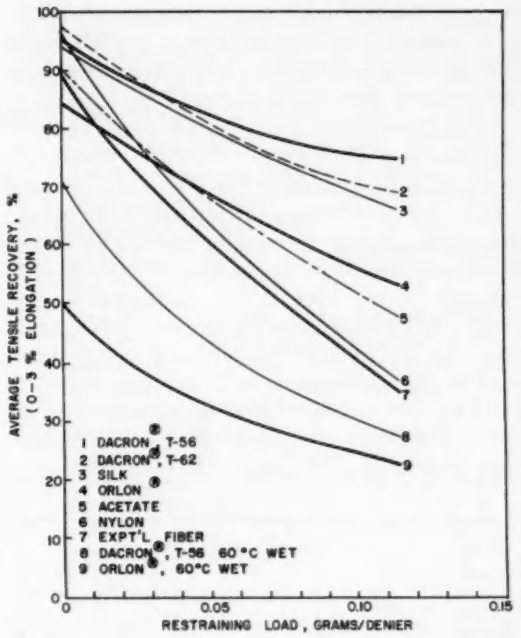

Fig. 4. Average values of restrained tensile recovery over the range of strains from zero to 3% versus the imposed restraint.

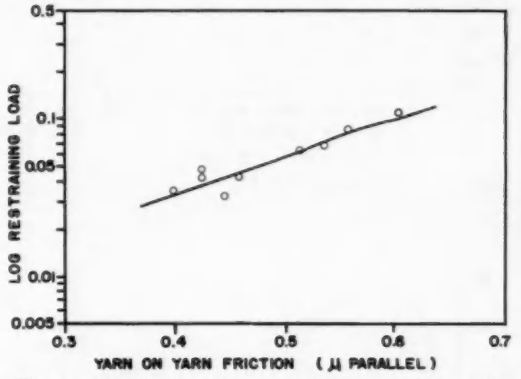

Fig. 5. Relationship between coefficients of fiber-on-fiber friction and the restraining loads at which the average restrained tensile recoveries equal the respective fabric wrinkle recoveries.

and Monsanto recovery shown in Figure 6 is obtained. Of course, an exact 1:1 correspondence would be shown in Figure 6 in the absence of any scatter about the $\log_{10}$ load-versus-μ curve, since such a correspondence was assumed in the first place in order to obtain that line. However, it is significant that *some* relationship between restraint and μ exists such that a high degree of correlation ($r =$

0.99) is found between a combination of the two yarn properties (average restrained tensile recovery and coefficient of friction) and fabric wrinkle recovery for a wide variety of fibers.

Discussion of Results

The tendency toward zero recovery for small strains and the differences with regard to the appearance of a maximum in recovery under load between nylon and Dacron shown in Figure 3 prompted an extension of the fabric-creasing experiments to include a wider range of strains imposed during creasing. By variation of the thickness of the spacer used in the Monsanto wrinkle recovery tester, recoveries from creases involving strains from 4% down to 0.25% were measured. Still lower levels were attained by wrapping swatches 180° around cylinders up to ½ in. in diameter and floating the fabrics on the surface of a pool of mercury during the recovery period. The resulting fabric recovery-versus-imposed strain behavior shown in Figure 7 exhibits all the qualitative features of the yarn recovery-under-load curves shown in Figure 3.

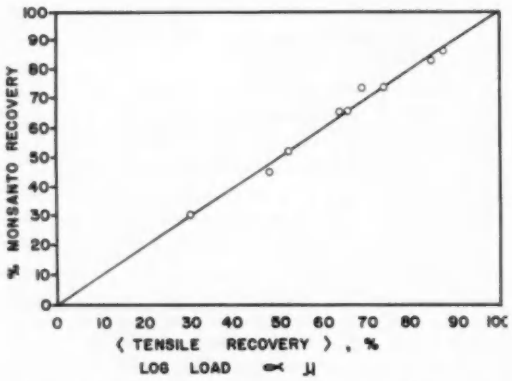

Fig. 6. Relationship between fabric wrinkle recovery and average restrained tensile recovery. The relationship shown in Figure 5 was assumed in determining the restraint.

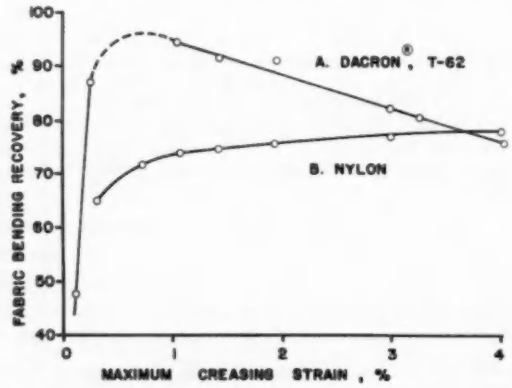

Fig. 7. Fabric bending recovery as a function of maximum fiber strain imposed upon creasing.

In going from tighter to looser types of construction, fabric recoveries for a given yarn are usually found to increase. This has been attributed to increased freedom of motion, so that fibers are able to assume configurations of lower strain. This was indicated by an experiment described by Hamburger et al. [6] in which the fabric crease-angle recoveries increased as cross threads were removed. A similar experiment was performed by the author on the fabrics used in this work. These results are listed in Table III, along with the average free tensile recoveries and the average tensile recoveries under a small restraining load.

It can be seen by comparing these fabric recoveries with those listed in Table I that all the fabrics with the filling threads removed exhibit greater recovery than the parent fabrics. While it is true that decreased strain via translation, twisting, or larger radius bending may raise recovery (see Curve A, Figure 7), the behavior of nylon indicates that this is not the only mechanism operating and probably not the principal one. It will be recalled from Curve B in Figure 7 that the fabric recovery of nylon decreased with decreasing strain, whereas the recovery of nylon fabric increased upon removal of filling threads. This suggests that removal of the filling threads considerably reduced the lateral forces holding the fibers together so that the fabric recovery approached the no-load or free-fiber bending recovery.

TABLE III. Effect of Filling-Thread Removal on Monsanto Wrinkle Recovery

	% Recovery		
Sample	Monsanto	Average tensile, 0.0075 g./den. load	Average tensile, no load
Dacron	92	94	95
Dacron, T-62	93	93	97
Experimental fiber	86	83	89
Nylon	90	90	96
Orlon	82	82	84
Acetate	86	86	90
Silk	90	91	94

Conclusions

A low order of fiber permanent set is a necessary but not sufficient condition for a high degree of fabric recovery from a bending-type deformation. The restraint arising from interfiber friction has been shown to be a factor which cannot be neglected in determining fabric recovery from isolated fiber recovery. Although the effect of friction is significant at all levels, it is particularly so at very low strains in which the restoring force within the fiber approaches the external restraint. Under these conditions, a completely elastic material would show low recovery.

Acknowledgment

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Note

The paper "Load-Deflection Analysis of Fibers with Plane Crimp" which appeared in TEXTILE RESEARCH JOURNAL **30**, 568 (1960) was a joint contribution from Textile Research Institute and the Department of Mechanical Engineering, Princeton University. This paper is a portion of the doctoral dissertation of R. Chicurel, formerly a Textile Research Institute Fellow.

The Torsional Properties of Single Wool Fibers

Part I: Torque–Twist Relationships and Torsional Relaxation in Wet and Dry Fibers

T. W. Mitchell and M. Feughelman

C.S.I.R.O. Wool Research Laboratories, Division of Textile Physics, Ryde, N.S.W., Australia

Abstract

An apparatus is described for the direct measurement of torque–twist relationships for single wool fibers. Calculation of the rigidity of a dry fiber (0% relative humidity) agrees with results obtained by Speakman, who used a torsion pendulum technique. However, this latter technique is shown to give an underestimation of the rigidity of the fiber at 100% relative humidity. This discrepancy is explained as being due to the hyperbolic relationship between the torque and twist of a single fiber. Measurements were also carried out on the torque relaxation of a single fiber, both wet and dry, at fixed values of twist. All the results obtained are consistent with a molecular model in which the matrix consists of a cross-linked polymer held together by a network of hydrogen bonds.

Introduction

The rigidity of single wool fibers has been obtained by Speakman [5] by measurement of the time of vibration of a torsion pendulum. The measurements were carried out over the complete range of relative humidities between 0% and 100%. Experiments have been done [2, 4] on the twisting and coiling of keratin fibers under various conditions. However, there has been no direct measurement of the torque–twist relationship of a single wool fiber under various conditions of regain, temperature, and rate of twisting or torque application.

In this paper a description is given of the experiments that have been performed in an attempt to fill this gap in our knowledge of the torsional properties of wool fibers. Torque–twist measurements were carried out on single wool fibers at a constant rate of straining and torque relaxation measurements at various twist levels. These measurements were limited by the nature of the apparatus to atmospheres of 0, 58, 90, and 100% relative humidity.

Experimental

In all the experiments described in this paper, the fibers were twisted at a constant rate at one end and the torque in the fiber measured by attaching the other end to a fine phosphor bronze strip of known torque per unit angular displacement. The dimensions of the strip were so chosen that the torque per unit angular displacement of the wire was about 100 times greater than the torque per unit angular displacement of a wool fiber in its most rigid state. This ensured that the angular movement of the wire, which is a measure of the torque, could be neglected relative to the twist in the wool fiber. The method of twisting of the fiber is illustrated in Figure 1. One end of the fiber (F) was attached with Araldite epoxy resin to the brass end piece (E), which was clamped to the revolving frame (R). This end piece (E) can be moved horizontally with respect to the frame so that the axis of the fiber could be adjusted to the center of rotation of the frame. The other end of the fiber was cemented to the brass weight (C) to which was attached the mirror (M). A phosphor bronze strip (P) 0.15 mm. × 0.03 mm. connected the brass weight (C) and the mirror (M) to the stationary frame (K).

To find the torque on the wool fiber the rotation of the phosphor bronze strip was measured with the aid of an optical lever system (Figure 2). Light from a point source (S) was passed through a converging lens system and reflected from a mirror attached to a small brass cylinder (C) at the bottom of the phosphor bronze strip (see Figure 2). The reflected light comes to a point focus on a drum (D) which can be driven at a range of constant angular

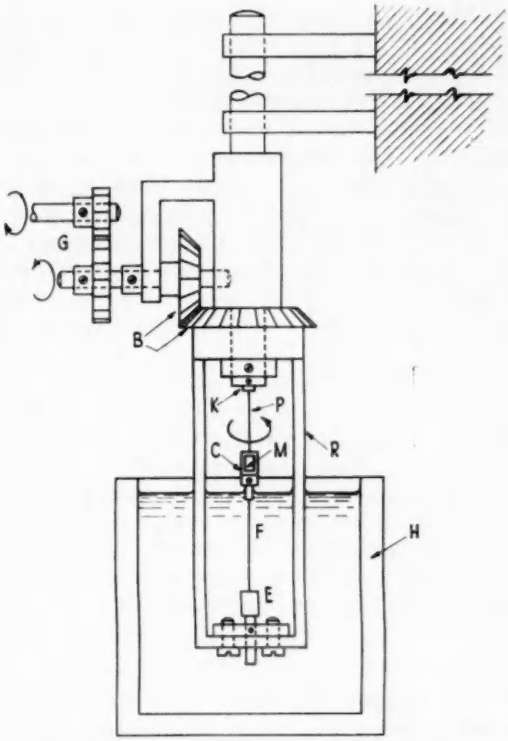

Fig. 1. Diagram of the twisting mechanism for the determination of the torque–twist and torque–relaxation relationships of wool fibers.

speeds about a horizontal axis. Photographic film was attached to the drum and used to record the movement of the light image focused on the drum. The horizontal movement of the light point on the drum represents the torque applied to the fiber. Because of the constant twist rate on the fiber and the constant rate of rotation of the photographic drum, rotation of the drum represents twist applied to the fiber. When the fiber was held at constant twist during torque relaxation tests, the rotation of the drum represents time.

The phosphor bronze strip used was 14.68 mm. long. The torque unit angular displacement of this strip was 30.2 dyne-cm./radian. This value was calculated by measuring the period of the torsion pendulum formed by this strip and the brass cylinder. The moment of inertia of the cylinder was calculated from its weight and dimensions. The distance of the mirror from the drum was 104.0 cm., which meant that a horizontal movement of the spot on the drum of 1 mm. corresponds to $30.2/(2 \times 1040)$ dyne-cm. torque on the wool fiber under test, i.e., to 0.0145 dyne-cm.

For 100% relative humidity the experiments were carried out with the wool fiber in water and for 0% relative humidity in Analar glycerol, while the 90% relative humidity experiments were performed in a suitably adjusted solution of triethylene glycol and water. It was found necessary to carry out all experiments in liquid medium to damp out random oscillations of the torsion-measuring mechanism. However, for 58% relative humidity the experiments were carried out in air at room humidity and, although oscillations occur in the torsion-measuring mechanism, the graphs were found to be acceptable. Further, when changes of temperature of the liquid were required, it was necessary to have the whole atmosphere around the apparatus at the same temperature as the liquid, to prevent convection currents in it disturbing the torsion measurement.

Three rates of twisting of the fiber were used: 5.74 radians/min., 13.82 radians/min., and 24.4 radians/min. Higher rates of twist were found to be impractical because of excessive disturbance to the torsion-measuring mechanism caused by the stirring of the liquid by the twisting mechanism.

Wool fibers used in the experiments, unless otherwise specified, were from penned Corriedale sheep hand-fed to obtain uniformity of fiber growth. The cross-sectional area along the length of fibers from these sheep gave a coefficient of variation of about

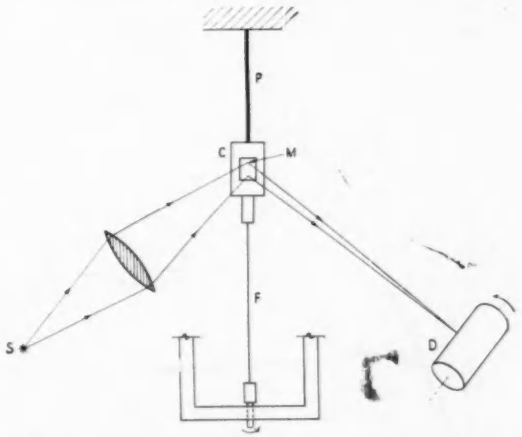

Fig. 2. Diagram of the optical lever system for the determination of the torque–twist and torque–relaxation relationships of wool fibers.

5%. The fiber length used was 25.0 mm. The fiber was attached at each end using Araldite epoxy resin. Great care had to be taken in setting the fiber in position so that the axis of twisting of the fiber passed through, in particular, the bottom point of attachment of the fiber; otherwise, during twisting, the circular motion of the point of attachment at the bottom of the fiber caused an undesirable oscillatory motion of the torsion-measuring mechanism.

Because of the permanence of the attachment of the fiber in the apparatus it was necessary to relax the fiber *in situ* after each mechanical test. After each test the fibers were relaxed in water for 1 hr. at 40° C. This relaxation technique was checked by consecutive tests for repeatability of torque–twist and torque relaxation both in water and dry. The calculated values of the rigidity modulus for repeated tests on the same fiber (see Table I) gave a coefficient of variation of individual values of approximately 4% for both dry and wet fibers. No significant variation of the torque–relaxation results was detected in these tests. The room temperature was 20° C.

The possibility that linear extension or linear stress which follows from the twist inserted in the fiber having an effect on the torque twist results was investigated. With a maximum twist of 70 radians the maximum linear strain (of a filament on the fiber surface) was only about 0.1%; i.e., the linear stress was very small. In separate experiments it was shown that strains of this magnitude had a negligible effect on the torque–twist curve.

TABLE I.

	η_D, Rigidity dry, dynes/cm.² × 10^{-9}	η_W, Rigidity wet, dynes/cm.² × 10^{-9}
	16.5	1.61
	16.2	1.47
	16.4	1.53
	15.7	1.45
	16.1	1.47
	14.9	1.44
	16.6	1.42
Mean	16.1	1.48

TABLE II.

Fiber no.	η_D, Dry rigidity, dynes/cm.² × 10^{-9}	η_W, Wet rigidity, dynes/cm.² × 10^{-9}	η_D/η_W
1	16.1	1.48	10.9
2	17.2	1.71	10.1
3	—	1.45	—
4	—	1.37	—
5	—	2.02	—
6	—	1.63	—
7	18.1	1.64	11.0
Mean	17.1	1.61	10.7

Results

Torque–twist measurements were carried out in water on seven wool fibers at a constant rate of twisting of 13.82 radians/min. The twisting was discontinued when a definite value of twist strain was reached; the fiber was allowed to relax at this strain, the torque being recorded continuously for times up to 2 hr.

At the end of the experiment the twist was re-

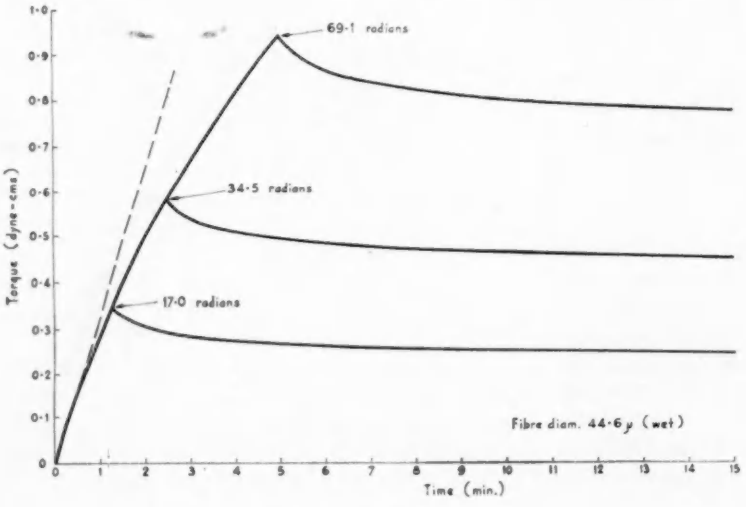

Fig. 3. Torque–twist curve at a constant rate of twisting followed by torque–time curves at three twist levels for a single wet wool fiber.

moved and the fiber relaxed in water at 40° C., as indicated previously. The torque–twist experiment was repeated up to a new level of twist strain and a new torque–relaxation curve at a higher twist strain was obtained.

A typical series of torque–relaxation curves and the accompanying torque–twist curve is illustrated in Figure 3. The torque–twist curve is not linear even near zero twist, and so a value of torsional rigidity was calculated using the torque per unit angular displacement determined by the tangent to the torque–twist curve at zero twist.

The rigidity η is given by

$$\eta = \frac{2l\mu}{\pi r^4} \qquad (1)$$

where μ = torque per unit angular displacement, l = length of the fiber under test, and r = radius of the fiber under test.

For the seven fibers an average value of 1.61×10^9 dynes/cm.^{2} was obtained for the rigidity of wet wool (see Table II). The individual values ranged from 1.37 to 2.02×10^9 dynes/cm.^{2}, which indicates the possible existence of a genuine difference from fiber to fiber. However, in the calculation of η (Equation 1) the radius enters as a fourth power, so that inaccuracy in measuring the radius is increased exponentially. Therefore it would be necessary to carry out many more measurements both on diameter and on other fibers before it could be assessed whether the range of the rigidity η obtained indicates a true variation of rigidity between individual fibers.

The shape of the torque–twist curve was found empirically to approximate closely a rectangular hyperbola

$$\frac{1}{T} = \frac{a}{\theta} + b \qquad (2)$$

where T is the torque and θ the corresponding twist on the fiber under test. a and b are constants, $1/b$ being the value of the torque to which the curve is asymptotic; i.e., the value of torque for $\theta = \infty$. $1/a$ is the value of the slope of the $T - \theta$ curve at zero twist. Figure 4 shows the plot for typical fibers of $1/T$ against $1/\theta$ showing the linearity of the relationship of these two parameters and hence the accuracy of the empirical Equation 2.

Typical torque relaxation curves obtained for one fiber at various twist strains are shown replotted in Figure 5. Here, the torque T_t corresponding to time t after commencement of the experiment is divided by the value of the torque T_{60} corresponding to $t = 60$ min. and the resultant value plotted against log t. For the wet fiber the proportion of torque relaxation in the period 0.3–60 min. reduces with increase of the twist strain at which the fiber is held.

Torque–twist measurements on some of the fibers were also carried out in Analar glycerol at a constant rate of twisting of 13.82 radians/min. The torque–twist curves for these dry wool fibers were

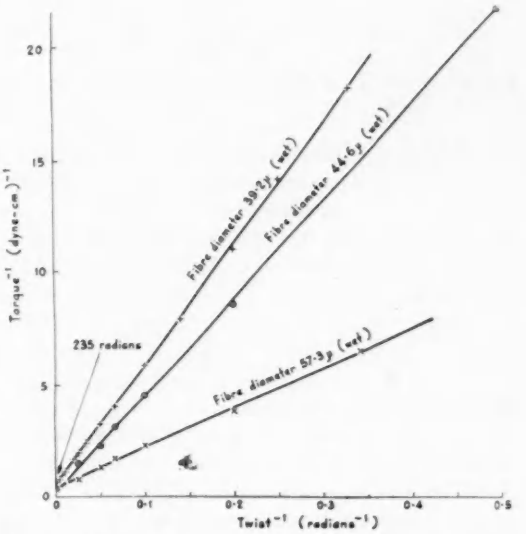

Fig. 4. Graph showing the relationship between $1/T$ and $1/\theta$ for three wool fibers in water.

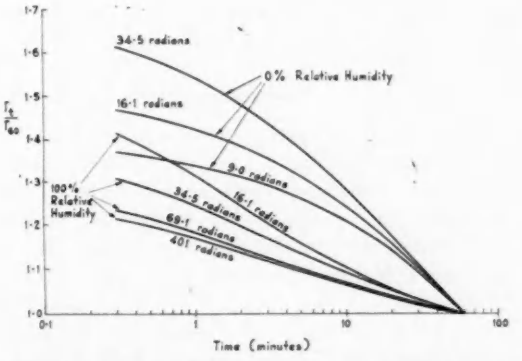

Fig. 5. The plot of T_t/T_{60} against log t for the torque–relaxation of wet and dry wool fibers at various twist strains. T_t is the torque corresponding to time t after commencement of the experiment; T_{60} is the value of torque corresponding to $t = 60$ min.

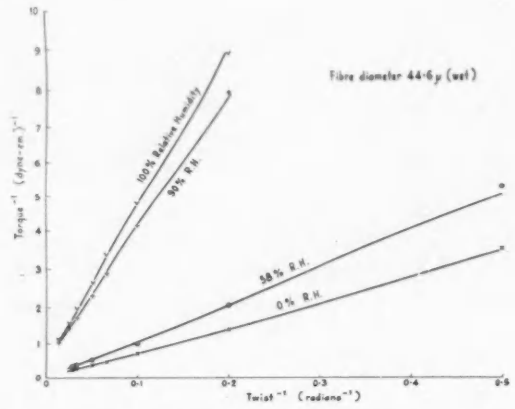

Fig. 6. Graph showing the relationship between $1/T$ and $1/\theta$ for a single wool fiber at various relative humidities.

shown again to follow an hyperbola of the same form as indicated in Equation 2 for wet fibers (see Figure 6). Measurements were also carried out on one fiber at 90% and 58% relative humidity. In all cases the form of the torque–twist curve is that of a rectangular hyperbola. The main change from dry to wet is the value of a in Equation 2. This quantity a is the slope of the lines in Figure 6.

Torque relaxation at various twist levels were obtained for fibers in Analar glycerol in the same manner as for fibers in water. Resultant sets of curves were similar in appearance to the curves obtained for wet fibers illustrated in Figure 3. Analysis of these torque–relaxation curves by replotting T_t/T_{60} against log time, as was carried out for the wet fibers (see Figure 5), showed that the proportion of torque–relaxation in the period 0.3–60 min. *increases* with increase of twist level. This is the opposite effect to that obtained for wet fibers.

Discussion

The modulus of rigidity of a dry fiber of 17.1×10^9 dynes/cm.^{2} as found from torque–twist results agrees well with Speakman's figure [5] of 17.6×10^9 dynes/cm^2. However, the mean value of 1.61×10^9 dynes/cm.^{2} for the rigidity of a wet fiber is significantly higher than Speakman's value of 1.2×10^9 dynes/cm^2. The cause of this discrepancy is easily understood when one considers the difference in the techniques. Speakman used a torsion pendulum and assumed a linear relationship between torque and twist. The true relationship, however, is hyperbolic. For wet fibers (or near 100% relative humidity), large twist displacements of the torsional pendulum would be necessary to obtain suitable restoring torques, and the torque per unit twist obtained by this experiment would correspond to the slope of the chord of the hyperbola at this twist. This would underestimate the initial torque per unit twist on the fiber. However, this underestimation would not occur for a dry fiber because the high value of torque per unit twist greatly reduces the twist necessary to obtain a suitable restoring torque, with the result that the difference in the slopes between the tangent at zero twist and the chord of the hyperbola is negligible. In a previous paper [1] it was predicted, from theoretical consideration of a two-phase structure, that the rigidity modulus of wet wool is approximately 2×10^9 dynes/cm^2. It is interesting to note that the value obtained in this paper of 1.61×10^9 dynes/cm.^{2} is much closer to this theoretical value than the result obtained by Speakman of 1.1 to 1.2×10^9 dynes/cm^2.

It should also be noted that genuine structural differences may exist between the wool fibers used by the authors and Speakman. These differences, e.g., difference of microfibril–matrix ratio or ortho–paracortex ratio, would show up in the wet fiber rather than the dry fiber, which acts mechanically as an isotropic homogeneous material [1].

The hyperbolic relationship between torque and twist holds extremely well even for high twists, as indicated in Figure 4. The results for a fiber of 39.2μ diameter (wet) which was tested to 235 radians twist show no visible deviation from linearity in the plot of inverse torque against inverse twist. This means that with increase of twist of the fiber the torque in the fiber approaches an asymptotic value of $1/b$. Averaged for the fibers tested and weighted for the fourth power of the diameter, the value of $1/b$ for a 50μ fiber is 3 dyne-cm.

It has been pointed out in a previous paper [1] that the torque on a fiber due to a twist is mainly due to the reaction of the matrix to the shear strain applied to it. If we regard the matrix as a cross-linked polymer held together by a network of hydrogen bonds, the following molecular picture of the structure in the matrix near zero twist and also under high-twist conditions is compatible with the results obtained. Initial twist strains hydrogen bonds in the network and, as the twist increases, some of these break. As the twist increases further, some of the broken hydrogen bonds re-form on new

sites, possibly *in a strained state*. Eventually, as a large value of twist is reached, the rates of breaking of hydrogen bonds and the formation of new bonds become equal and further twist does not produce an increase of torque. The matrix under these conditions is acting as a viscous solution and presumably would continue in this way with increasing twist until the cross links and the backbone structure of the polymer forming the matrix became extended, or the deformation of other physical entities in the fiber, such as the microfibrils, introduced opposition to the twist.

On the basis of the above molecular model, if twisting is suspended, for small twist values the relaxation of the torque with time will be due wholly to the breakdown of hydrogen bonds. However, for large values of twist, when twist ceases, not only do hydrogen bonds break with time but other hydrogen bonds may be formed in a strained state which *add* to the torque. Hence for high-twist values the proportion of torque relaxation may be expected to be lower than for small twist values. As mentioned previously, this phenomenon was observed for wet fibers.

For dry fibers, however, this is not the case. This again can be understood in terms of the molecular model. For dry fibers the whole fiber acts as an isotropic material with hydrogen bonds many times stronger than in the wet fiber. Initially on twisting, the hydrogen bonds are strained but, because of their higher strength, do not break as easily as in water. In the absence of water and hence the lack of mobility of the chains, re-formation of hydrogen bonds (in particular, strained bonds) is probably absent. This would result in the torsional stress–relaxation proceeding more rapidly with time because of the lack of formation of strained hydrogen bonds *adding* to the torque. With increased torque, subsequent to increased twist (hence greater force on individual hydrogen bonds) the rate of breakdown proceeds more rapidly. Hence the greater proportion of stress–relaxation at higher twist levels, as indicated on Figure 5.

The concept of formation of strained hydrogen bonds has been proposed and demonstrated elsewhere under different circumstances [3]. However, there does not seem any valid reason why they should not exist also under the conditions quoted in this paper.

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New Developments in Polyvinyl Alcohol Fibers[1]

Richard D. Wells

Air Reduction Chemical Company, A Division of Air Reduction Company, Inc., New York 17, New York

and Henry M. Morgan

Fabric Research Laboratories, Inc., Dedham, Mass.

PROBABLY the most significant "new developments" in pva fibers are that engineering plans for a full scale American pva fiber plant are now actually nearing completion and that the companion market studies have advanced to the stage of active market development. This awakening of commercial interest in pva fibers is of course based on related technological developments. Though this technology has advanced by stepwise increments rather than by revolutionary breakthrough, it has pushed pva fiber across several critical thresholds and into many promising fields of application.

One may ask why "vinal" (FTC generic for pva fibers) has not been on the American textile scene before now. Certainly the attributes of pva as a fiber-former were recognized quite early in the history of synthetic polymers. Several chemical fiber interests here have conducted pva fiber development and evaluation projects at various times. Vinal has gained considerable commercial success abroad, in a variety of important applications and in competition with most fiber types with which it would contend here. To quote recent comment in the journal *Man-Made Textiles:* "Why this fiber with its outstanding properties is confined to Japan is difficult to understand."

Since public record sheds little light on this question, only general assumption can be offered. It seems a safe conjecture that pva may have appeared a rather expensive material for a hydrophilic fiber. The trend in synthetics has been strongly toward more hydrophobic fibers for both apparel and industrial uses because synthetics in general seemed to be doing best in applications where the high moisture sensitivity of the natural and cellulosic fibers showed to maximum disadvantage. Perhaps the potential strength and ruggedness of pva fibers had not been fully assessed, or certain markets were not yet ready for vinal's particular combination of properties. Possibly vinal would have been in conflict with other fiber programs on which heavy commitments had already been made. Whatever the reasons, vinal has remained a sort of "sleeper" in the fiber field here and in Europe until quite recently.

Where does vinal fit into the ranks of fiber types? Isn't there already a surfeit of variety? What does vinal offer that is not now at hand?

Since vinal does not have a close counterpart for ready reference, it may help to put it into perspective by taking note of two converging trends in fiber development.

Viewing the textile fiber field broadly we see continuing effort to alter the natural and cellulosic fibers to decrease moisture sensitivity, add strength or resilience, or increase resistance to chemical and microbiological degradation. These modifications are aimed to provide some measure of those very properties on which the synthetics have gained their advantage and acceptance, and the developments continue, though frequently there are inherent limits as to degree of attainment, sacrifice of other properties, or reduction in basic economic advantage.

From the other side we see a beginning trend to diversify the synthetics into forms more pleasing in moisture and tactile characteristics, more adaptable to processing and fabrication, more generally acceptable along the familiar lines which (other than price) have been the main defensive strength of the natural and cellulosic fibers in the competition among fibers.

From this view of these efforts to toughen up the more fragile fibers and to tame down the more rugged fibers, one may gather that there is a place for vinal. Vinal appears to fully span the otherwise still wide gap between the two fiber groups which are at the extremes. It can match tenacity with the best in the league, and yet has the moisture capacity and softness needed for full comfort in wearing apparel.

[1] Presented at the 30th Annual Meeting of Textile Research Institute, New York City, March 25, 1960.

Vinal has the chemical and rot resistance one expects of the synthetics, yet adapts to processing, dyeing, coating, and compounding with a facility quite unlike the stubborn inertness of the more common synthetics. Here is a new combination of several significant fiber properties, with little if any compromise of any of these properties.

Vinal's particular combination of properties is not necessarily the magic formula for all applications, of course. In some uses one or more of these properties may be relatively meaningless, beyond any practical need, or actually detrimental. There are other applications where vinal may be ideal as to all factors of function, but which are subject to economic factors limiting its commercial acceptance. Vinal's properties do, however, justify serious consideration in a host of likely textile applications.

In discussing these properties it must be pointed out that the term "vinal" encompasses a growing family of rather distinct subtypes, derived through several fiber-forming procedures and diversifiable by a number of modifying techniques. This presentation is necessarily confined, in mentioning specifics, to two of the vinals which the Air Reduction Chemical Co. has selected as the most logical prototypes for its proposed initial commercial fiber program.

Vinal 5F

The first of these is a wet-spun type which we refer to as vinal 5F. It is made by a system which roughly follows rayon technology, with sequential stages of coagulation, drawing, heat treating, and formalization to develop and harden the fiber structure. This and some chemical modifications of it, in deniers and staples for various mill systems and in tow for direct conversion processes, has been the main commercial vinal type so far. Current production by the Kurashiki Rayon Co. alone exceeds 30 million pounds a year and is growing steadily, and somewhat similar vinals are moving through pilot into commercial stages elsewhere. Specific applications were discussed in an earlier paper at the AATT, which has since appeared in *Modern Textiles*. Vinal 5F has found applications in about every product where cotton has been traditional but where modern use and economic requirements dictated a major upgrading of performance levels in strength, abrasion resistance, and chemical and rot resistance. The list includes fish nets, hose and belting, bicycle tires, footwear, tarps and covers, underwear, socks, thread, and work, school, and sports clothing. A big advantage to vinal is that it can be introduced easily into about any going cotton mill, finishing, fabricating, or combining system, with no need for new techniques or equipment.

Vinal 5F has a definite skin–core structure, as evidenced in Figure 1. The present standard version has this somewhat dogbone shape. More cylindrical cross sections are attainable and are beginning to be made for certain applications where roundness has demonstrated important advantages.

Typical fiber properties are shown in Table I. Vinal 5F most definitely should be classed among the high-strength fibers. Initial modulus is high, average stiffness medium, and elasticity low. Moisture regain and capacity are in the range of cellulose acetate. Abrasion resistance is not shown for lack of standard index, but in practical applications it can be considered at least twice that of cotton and approaching that of the polyesters.

The typical stress–strain curve for vinal 5F is shown in Figure 2. It is practically a straight line

TABLE I. Vinal 5F Physical Properties

Standard tenacity	4.5–6.0 g./den.*
Wet tenacity (% of dry)	80–85%
Standard elongation	17–22%
Tenacity at 5% strain	1.0–1.7 g./den.
Elastic recovery at 5% strain	50–60%
Average stiffness	30–40 g./den.
Modulus	45–65 g./den.

*Values vary with fiber denier.

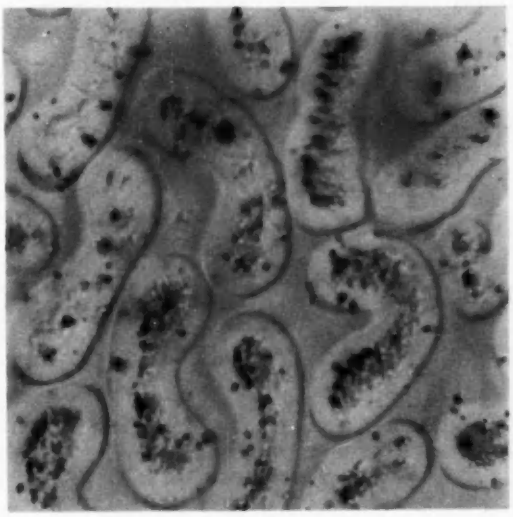

Fig. 1. Cross sections of vinal 5F.

with a slight yield point at about 2% strain, with little evidence of plastic flow but much of strain hardening.

While the dry heat characteristics are excellent with no real evidence of thermoplastic flow, vinal 5F is plasticized somewhat by water at elevated temperatures, as indicated by Figure 3. The resulting lowering of stiffness and rupture tenacity has little significance in the normal conditions of processing and use, but the hot-wet plasticity does have bearing on such matters as pressure dyeing or direct steam sterilization or vulcanizing. In the process drying of fabrics containing appreciable vinal 5F, moisture should be reduced gradually at first, as by lagged or low-pressure drying cans, to avoid unwanted stretch or subsequent stiffening. In a few cases, however, advantage may be taken of this for special effects.

There are so-called "soluble" vinals, of which we have several under active evaluation. One use of these, in various solubility temperatures from 80° C. and up, is as binder fibers in papers and nonwovens. By proper control of time, temperature, moisture, and pressure variables in a drying operation, it is possible to achieve a high degree of spot-contact bonding, as evidenced in Figure 4, and still preserve the integrity of the bonding fiber as a high-strength structural member. The practical implications are obvious.

The use of the soluble vinals as temporary spacer, re-enforcing, or separator elements has been discussed in earlier presentations, but again it should be pointed out that in practice these may not always disappear into solution quite as rapidly or completely in the practical application as they do in the test beaker, since rather surprisingly small tension forces raise the effective solubility temperature appreciably. A more recent development in soluble vinals are the vinyl and allyl copolymers, which make possible fibers with solubility temperatures as low as 30° C. or less with standard tenacities still in the 3 g./den.

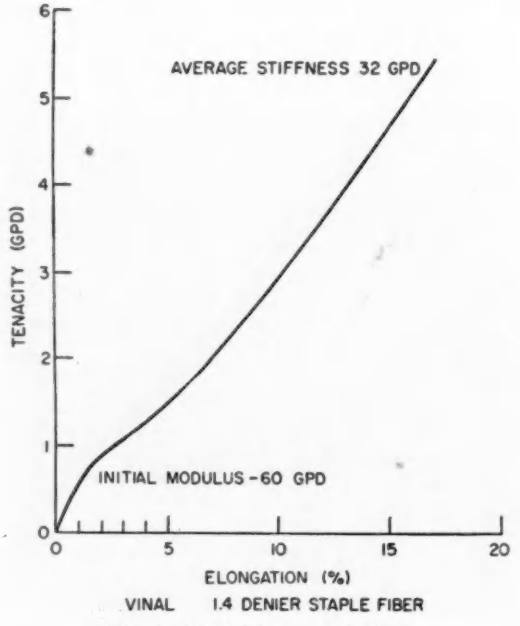

Fig. 2. Vinal 1.4-den. staple fiber.

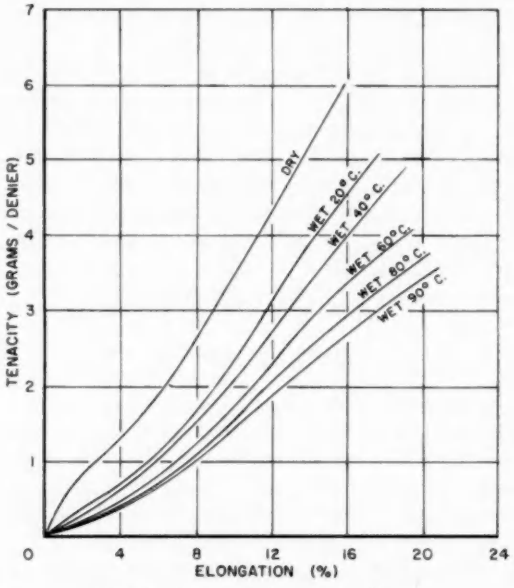

Fig. 3. Vinal 1.4-den. staple fibers.

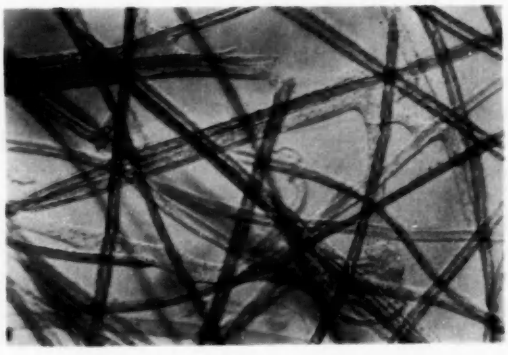

Fig. 4. Soluble vinal with vinal 5F.

range. It may be assumed that a whole range of "soluble" vinals will be available, tailored to suit the individual requirements of the various applications.

Further discussion of vinal 5F processing and applications is given in papers which appeared in *Modern Textiles,* November 1959. It is possible now, however, to add more positive information on weather resistance. (This information refers also to the type of vinal (FO) to be discussed next.) Our own data now confirm what had been earlier indicated broadly but not conclusively in earlier reports, and vouched for by years of practical service in outdoor conditions: the weather resistance of vinal is of a high order. In comparative tests in hot-dry, hot-wet, and an atmosphere of heavy general industrial contamination, bright vinal stood up as well as anything. In exposure times producing degradation in the 20–60% range for the samples in the series, the bright vinal showed clearly better durability than cotton, bright polyester, saran, and regular nylon, and was fully equivalent to the light-resistant nylon and superior in the hot-dry exposure.

Vinal FO

The versatility of polyvinyl alcohol as a fiber-forming material is exemplified by the continuous filament high-strength yarn referred to as vinal FO, also developed by the Kurashiki Rayon Co. This yarn is spun from polymer chemically similar to that used for the wet-spun staple fibers described above, but the similarity ends there. Vinal FO in multifilament and monofilament form is produced by a "semi-melt" process with a partial solvent to reduce the melting temperature. The filaments are hot drawn and heat treated after extrusion, with no subsequent formalization. The resulting vinal FO filament is a highly oriented, highly crystalline form of pure polyvinyl alcohol.

This new development, plus the polyvinyl alcohols produced from syndiotactic haloacetates, has contributed to the current reawakening of interest in pva as a fiber. Thus, before discussion of the physical properties of vinal FO yarn, a brief review will be given of some of the features of the structure of pva. As a specific example, vinal FO filaments will be used.

Bunn has shown that the hydrogen and hydroxyl groups are interchangeable in the crystal structure of pva. While the hydroxyl groups are considerably larger than the hydrogen, they are both small in comparison with the crystal spacings. Thus, stereo regularity is not required for the crystallization of pva. The isotactic (Figure 5a), syndiotactic (Figure 5b), and atactic (Figure 5c) forms have the same crystal structure. It is not surprising, therefore, that a highly crystalline fiber can be made from an atactic polymer.

Values of crystalline density of 1.348 g./cc. and amorphous density of 1.265 g./cc. have been reported for pva. Vinal FO fibers have a density of 1.320 g./cc. measured in a xylene–carbon tetrachloride gradient column. This indicates a degree of crystallinity of over 65%.

The high degree of crystallinity is achieved by physical conditioning, i.e., hot drawing and heat treatment. A consequence of the increased crystallinity is a great increase in hot water resistance. Kawakami and Soto have investigated the effects of various heat treatments on wet-spun pva fibers and have produced sample fibers with a degree of crystallinity of over 70%. They also studied the effect of these treatments on hot water shrinkage, and showed that with increasing heat treatment the crystallinity reached a maximum of 70% followed by a decline to 65%. However, the hot water shrinkage (80–95° C.), which hitherto had been considered to depend solely upon the degree of crystallization, continued to decrease with heat treatment without correlation with crystallinity *per se*. They suggest that

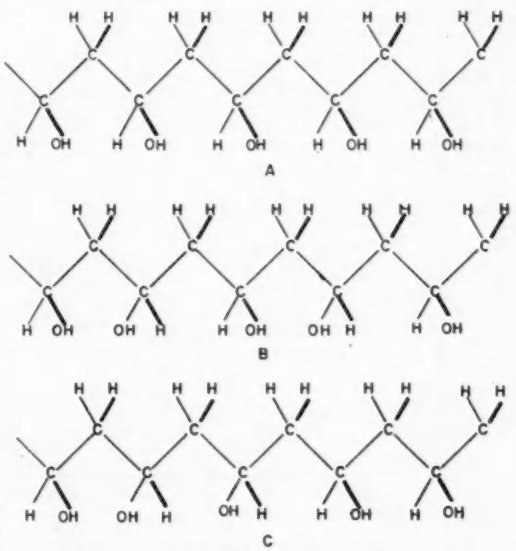

Fig. 5.

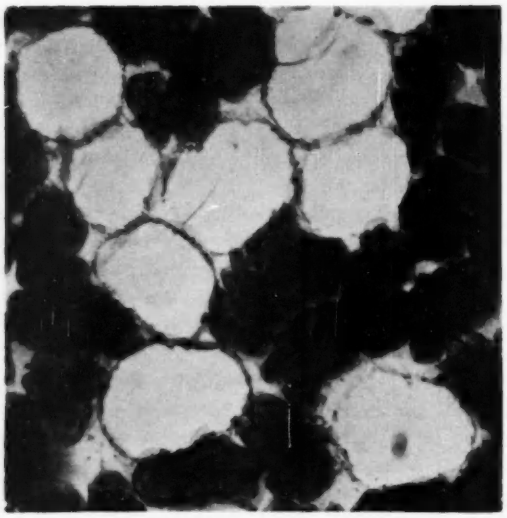

Fig. 6. Cross sections of vinal FO.

Fig. 7. Longitudinal view of vinal FO.

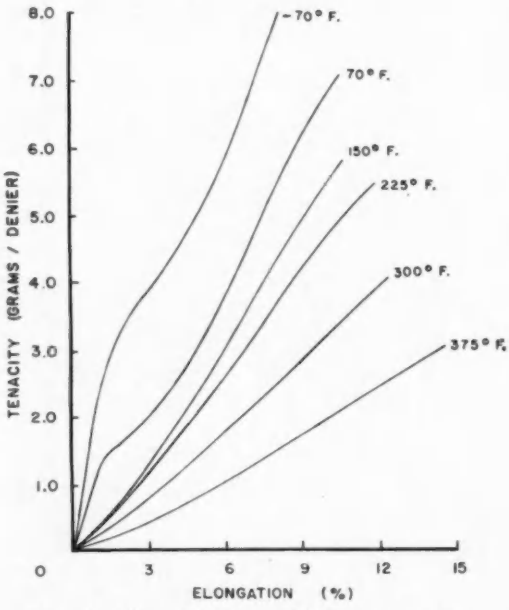

Fig. 8. Vinal 1200-den. multifilament, tested at various temperatures.

the disagreement between the hot water resistance and the degree of crystallization may be attributed to the differences in the network structure of the noncrystalline part of the fibers. In other words, the heat treatment which further reduces hot water shrinkage does so by modifying the amorphous material at the expense of some crystallinity.

Attempts at increasing the hot water resistance of pva have recently been reported using an entirely different approach. Haas, Emerson, and Schuler have prepared films of pva derived from polyvinyl trifluoroacetate. Certain of these films showed high degrees of hot water resistance and it was inferred that this was the result of stereo regularity. More recently, Fordham, McCain, and Alexander have prepared pva films from other haloacetates. These films were stated to be largely syndiotactic. Their results substantiated the findings of Haas et al. that high degrees of water resistance could be achieved. Unfortunately, we have no report of the crystallinity of these samples derived from vinyl haloacetates instead of the more usual vinyl acetate. Thus, it is not possible to assess whether the hot water resistance is produced because of increased order and hence crystallinity or whether the amorphous regions are less soluble because of the stereo regularity.

The high degree of orientation of the vinal FO fibers can be detected by x-rays and also by birefringence measurements. The high values of birefringence (0.038–0.040) are the result of a combination of the crystalline and amorphous orientation plus the form birefringence of the crystals. The importance of high orientation produced in the hot draw is to get a high-strength yarn.

It has been shown by Hirabayashi that pva fibers are composed of fibrils with microfibrils within them. It has further been shown by Hess that microfibrils of a pva fiber are in turn made up of crystalline and noncrystalline phases. Such a fibrillar structure is not peculiar to vinal FO filaments nor to pva fibers, but is common to all oriented fibers, natural, regenerated, or synthetic. Hirabayashi, however, has shown that with pva fibers, the spinning method influences the size and type of the substructure. The semi-melt process gives the finest fibrils, which in turn consist of extremely fine microfibrils. The fibrils range from about 1μ diameter to a few millimicrons in size. The finer microfibrils found in the oriented semi-melt fibers are evidently desirable, since

vinal FO has not shown any tendency to fibrillate in use.

Figure 6 shows the cross section of some of the filaments from a 1200-den., 200-filament vinal FO yarn. (The section was cut with the filaments intermingled with dyed viscose fibers.) An interesting consequence of the presence of the partial solvent in the semi-melt is that a thin dimpled skin structure forms when the fiber coagulates. These dimples are drawn out into longitudinal grooves which can be seen in both the cross-sectional view and in a longitudinal view, Figure 7, of a metal-shadowed fiber. This textured surface no doubt accounts in part for the good adhesion of these fibers in coating and dipping applications.

The combination of high crystallinity and high orientation produced by hot drawing give vinal FO filaments a high tenacity and a high modulus. Single filament tenacities average above 9 g./den. at standard conditions of temperature and humidity. The tenacity–elongation behavior is characterized by a high initial modulus of above 100 g./den. and a slight yielding at about 1.5% elongation, followed by strain hardening and linear stress–strain curve at high loads. Typical yarn property data are listed in Table II.

The melting temperature of dry pva is above 430° F., which is high enough for most commercial uses. Perhaps more important than the melting point is the tensile strength retention at elevated temperatures. Tensile properties of 1200-den. vinal filament yarn at various test temperatures are shown in Figure 8. At a test temperature of 300° F., for example, vinal FO still has tenacity of 4.0 g./den. and an initial modulus of 30 g./den. The stress–strain curve at elevated temperatures becomes essentially linear. These temperature characteristics are favorable for good behavior under such conditions as are met in tire curing. Vinal FO filament retains its modulus advantage over nylon throughout the useful temperature range.

The water resistance of vinal FO can also be seen from the tensile behavior in water at various temperatures (Figure 9). At room temperature there is little effect due to water, and adequate strength is maintained up to 90° C.

When considering a fiber for industrial use such as tire cord, the behavior under impact conditions becomes important. The three curves of Figure 10 show the effect of the rate of elongation on tensile properties of vinal FO. The lowest curve is representative of a normal slow rate of elongation with the Instron Tensile Tester, 10-in. sample length, and 2 in./min. extension speed. The middle curve is the result of testing on a pneumatic piston tester, 3-in. sample length, 8.3 ft./sec. extension speed. Vinal FO shows the classical viscoelastic response to increasing strain rates, i.e., a stiffening of the stress–strain curve with an increased rupture tenacity. The uppermost curve was calculated from a lateral impact ballistic test where the yarn was struck at 1000 ft./sec. Because of the shock wave loading which occurs

TABLE II. Vinal FO 1200 den./200 filament

Tenacity at 65% RH-70° F.		7.2 g./den.
Tenacity wet-70° F.		7.0 g./den.
Elongation at 65% RH-70° F.		10%
Elongation wet-70° F.		14%
Tensile modulus		160 g./den.
Average stiffness		72 g./den.
Toughness		0.34 g.cm./cm.den.
Birefringence		0.04
Specific gravity		1.32
Elongation, %	Load, g./den.	Tensile recovery, %
3	2.1	87
5	3.0	75
10	6.8	63

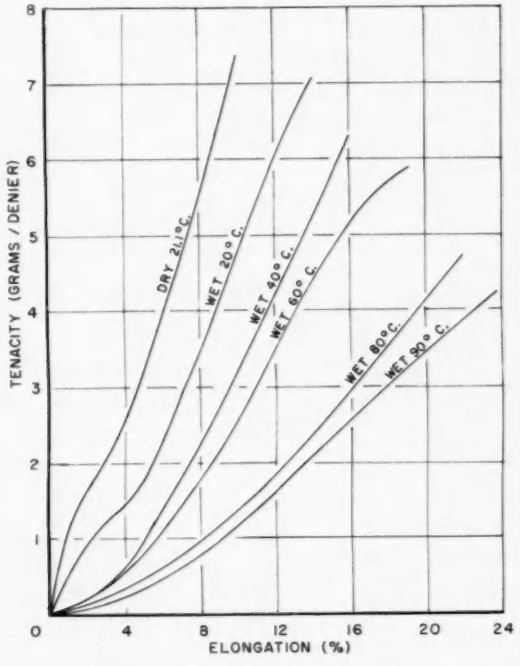

FIGURE 9 VINAL FO-1200 DENIER

Fig. 9. Vinal FO, 1200 den.

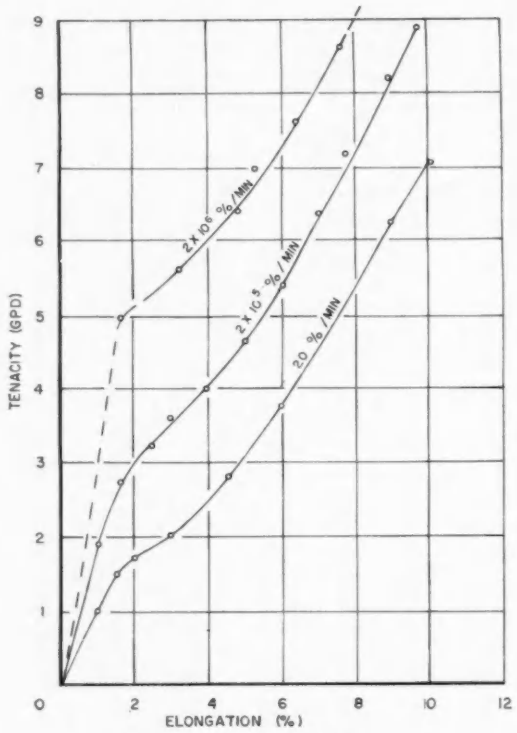

Fig. 10. Vinal FO, 1200 den.

at these velocities, it is difficult to ascribe a definite strain rate. However, the strain rate has been estimated at 2,000,000%/min. Even at the conditions of impact at high speeds, there is no decrease in the strength. This fact suggests that vinal FO will give full protection against road shocks when used as a tire cord.

Another interesting sidelight of the impact tests is the substantial increase in initial modulus which results from the increased strain rate. Under lateral impact at 1000 ft./sec the initial modulus is difficult to define, but it approaches the elastic modulus of 420 g./den. measured by sonic pulses (Pulse Propagation Meter).

The data presented here relate to vinal FO yarn, in the form which is now being used for tire cord. These same properties apply with apparently equal appropriateness to many other important industrial applications, particularly to those in which dimensional control under service conditions is as critical as ultimate strength. Since many of these applications also require thorough bonding of fiber to coatings or matrices, vinal FO has much to recommend it.

For uses where extreme high modulus and low extensibility are less favorable, for instance in items where very high twists are essential, vinal FO subtypes of almost equal ultimate tenacity but more compliant stress–strain characteristics are attainable.

In fact, from the point of view of general technological interest, perhaps the most intriguing aspect of the vinals is the versatility of the pva system. It would seem possible to tailor-make a vinal type to meet about any reasonable specification.

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Reversible Crimp in an Acrylic Fiber[1]

Elija M. Hicks, Jr., James F. Ryan, Jr., Robert B. Taylor, Jr., and Robert L. Tichenor

Textile Fibers Department, E. I. du Pont de Nemours & Co., Inc., Wilmington 98, Del.

THE BEHAVIOR of wool has long been recognized as unique and outstanding among natural fibers. Wool exhibits a very high degree of crimp which is important to its tactile properties. It exhibits a "live" behavior in finishing and wet-processing through a reversibility of crimp—crimp decreasing when the fiber is wet and returning to the original level upon drying. It has a high degree of bulk, resulting from its three-dimensional crimp structure. Menkart and Detenbeck [10], of Textile Research Institute, have related bulk of wool directly to the degree of crimp, and L. G. Ray, Jr. [13], of the Du Pont Company, has conducted studies emphasizing the influence of such fiber characteristics upon aesthetics. These particular properties of crimp and high bulk have long been the aim of man-made fiber producers.

Many investigators have studied the source of the behavior of wool. There is general agreement that the initial crimp in the wool fiber results from growth in a twisted follicle. There has been much less unanimity of opinion as to the origin of crimp reversibility. Several observers have noted the response of the wool fiber to moisture with the reversible crimp evident. The study of response to a number of physicochemical conditions has been carried out. As long ago as 1886, MacMurtrie [8] observed the differential swelling from side to side of wool fibers in potassium hydroxide solution and faithfully recorded this in sketches, although the point was not discussed. Woods [16], in 1935, studied the twisting and curling of wool in water. Berg [1] studied the twisting and curling in steam. Both of these studies were aimed at indicating the cause of the twisting and curling. Freney [5] extended the studies with sodium hydroxide solution and noted changes in twisting and curling with time.

It remained for Horio and Kondo [7] to reveal a definite structural asymmetry of wool fibers which could be correlated with their coiling and crimping nature. They used staining techniques under precisely controlled conditions of pH. These investigators showed a difference in dye receptivity for the two sides of the wool fiber (Figure 1). They also correlated this differential dyeing with the coiling and crimping nature of wool. Thus, they related a structural asymmetry or bilateral structure to the crimping and coiling of wool.

The true bilateral structure of wool was fully documented by a classicial study at Textile Research Institute. Mercer [11], in 1953, provided direct chemical evidence that wool cortex is made up actually of two parts, which he referred to as ortho- and paracortex. He treated wool fibers with peracetic acid, which dissolved a portion of the structure through rupture of disulfide cross-linkages. Using microscopic techniques, he noted that fibrils remained on only one side of the cortex (Figure 2). After the removal of the orthocortex portion from supercontracted fibers, he found that the paracortex was present in spiral form within the cuticle sheath. He noted that wool is unique in its fine crimp and that only wool, of all hair fibers, shows asymmetry of cortex. Continued work at Textile Research Institute by Mercer, Golden, Jeffries, Whitwell, Dusenbury, Wakelin, Coe, and Menkart [2, 4, 6, 9, 12] completed the monumental task of confirming the bilateral structure of wool on the basis of the ortho–para concept. This work is summarized ably by Dusenbury and Menkart [3] in the Proceedings of the International Wool Textile Research Conference held in Australia in 1955.

As a principle, it appears logical that if a bilateral structure could be accomplished in a synthetic fiber and if these components responded properly to physicochemical conditions, a combination could be made in one fiber of properties of a synthetic with the characteristics typical of wool. In earlier work, Sisson and Morehead [14, 15], of American Viscose,

[1]Presented at the 30th Annual Meeting of Textile Research Institute, New York City, March 24, 1960.

produced crimped rayon by the two-component approach. On a commercial basis, Fiber E filament yarn and a crimped staple made by Du Pont involved a degree of bilateral structure in a rayon. In these structures, the bilateral character was used to advantage to develop crimp (as, for example, in a sodium hydroxide boil-off), but aesthetic properties obtained were not of the same order as for wool.

As a result of research work carried out over the past few years, it has been possible to develop bilateral structure in an acrylic fiber. A commercial version of the fiber (now trademarked "Orlon Sayelle"[2]) was announced last fall as "Orlon" 21 acrylic fiber, but no reference was made to its bicomponent character. First public reference to the bilateral nature of this acrylic fiber was made by J. H. Dillon in a talk to the annual meeting of the Thread Institute last October.

Two-component filaments have been produced within the acrylic polymer system in the denier range of normal apparel fibers (3–6 den./filament) with structure tailored to respond to physico-chemical conditions such as heat and water. The components involve unique chemical modification of acrylonitrile polymers to achieve differential properties across the fibers. It is quite obvious also that unusual engineering requirements had to be met, since the filaments involved have diameters less than one thousandth of an inch. Novel equipment of high precision had to be developed for the job.

In appearance, the fiber differs significantly in cross section from conventional Orlon acrylic fiber.

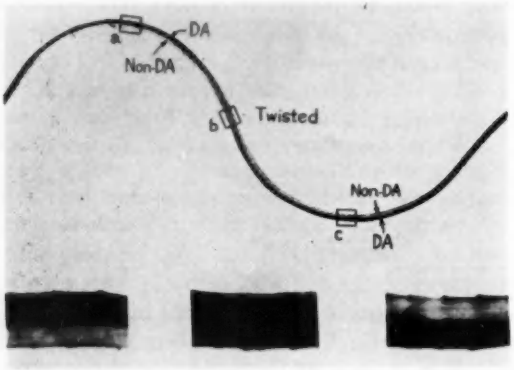

Fig. 1. Differential staining of wool fiber (per Horio and Kondo).

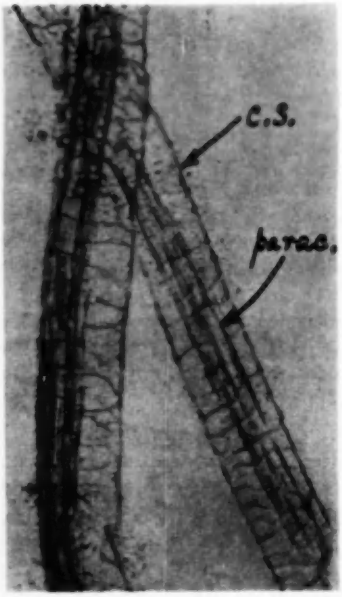

Fig. 2. Paracortex in wool fiber (per Mercer).

[2] Du Pont trademark.

Fig. 3. Cross sections of bilateral acrylic fiber and of wool.

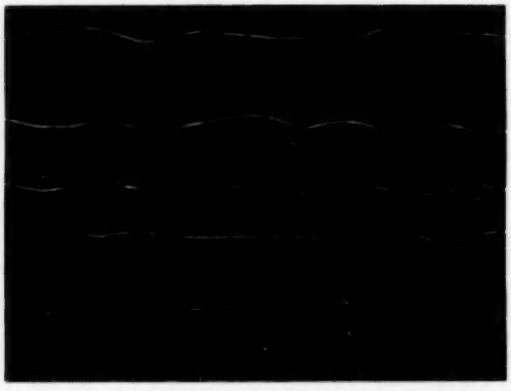

Fig. 4. Crimp in bicomponent acrylic fiber as produced.

The cross section is rather acorn-shaped (Figure 3), instead of the familiar dogbone shape, and is not unlike wool in this regard. The two segments of the cross section are clearly distinguishable. In longitudinal appearance, as the fiber is produced, there is a mild three-dimensional crimp (Figure 4).

The physical properties of the bicomponent fiber, as given in Table I, are quite similar to those of conventional Orlon acrylic fiber. Tensile properties, initial modulus, and transverse properties fall in the normal range for Orlon. Moisture regain of 2.6% at 65% relative humidity is about 1% above that for current Orlon. Table II presents the dependence of moisture regain on relative humidity. The bicomponent Orlon fiber exhibits a low regain over the complete range of humidities.

Far more important than the fiber appearance and physical properties is the way it behaves. First, considering its response to heat, it is found that one side of the fiber shrinks more under heat than does the other. The immediate result is a high degree of three-dimensional spiral crimp. It is evident that the nature of the crimp is quite similar to wool and entirely different from the mechanically induced crimp in most synthetics (Figures 5 and 6). The crimp develops very readily in typical processing operations, such as boil-off or dyeing procedures, followed by drying.

A second response of the fiber is its "live" behavior on wetting and drying. One side of the fiber swells more than the other. The side which has shrunk more on heating swells more with water and actually elongates, thereby decreasing crimp. Recrimping occurs as water is removed by drying (Figure 7). This crimp reversibility gives a fiber which wet-works or squirms during finishing. This wet-working constantly renews the original configuration of the fiber after initial crimping. In addition, it gives some degree of fiber intertwining for added cover in fabrics, but without felting action.

TABLE I. Fiber Physical Properties at 70° F. and 65% RH

	Orlon Sayelle*	Type 42 Orlon†	Wool‡
Dry tenacity, g./den.	2.3	2.3	1.5
Dry elongation, %	48	28	28
Wet tenacity, g./den.	1.8	1.7	1.2
Wet elongation, %	70	32	40
Loop tenacity, g./den.	1.6	1.6	1.1
Loop elongation, %	14	17	18
Initial modulus	38	35	27
Moisture regain, %	2.6	1.7	15
Specific gravity	1.18	1.14	1.32
Fiber stick temp., ° C.	250	255	—

* Trademark for Du Pont bicomponent acrylic fiber.
† Trademark for Du Pont acrylic fiber.
‡ Average 25 samples—58's to 70's wool.

TABLE II. Orlon Sayelle * Moisture Regain vs. Relative Humidity at 70° F.

% RH	Moisture regain, %
30	0.7
60	2.1
65	2.6
80	3.5
100	4.6

* Trademark for Du Pont bicomponent acrylic fiber.

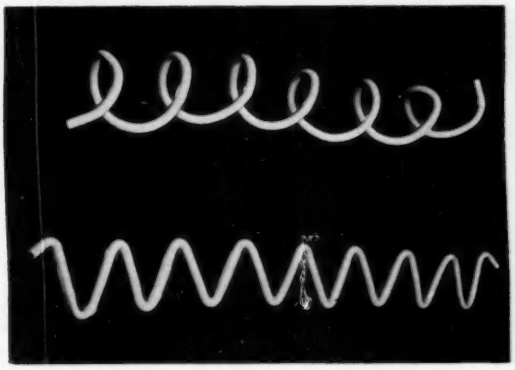

Fig. 5. Model of three-dimensional spiral crimp typical of bicomponent acrylic fiber compared with two-dimensional crimp of usual synthetic fibers.

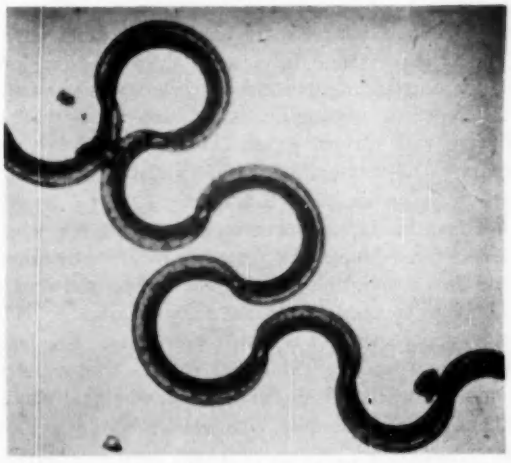

Fig. 6. Longitudinal section of differentially dyed bicomponent acrylic fiber.

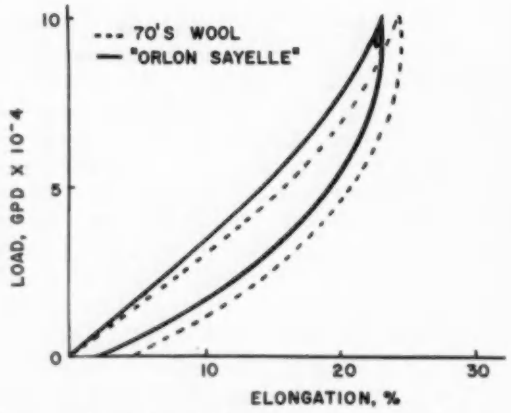

Fig. 7. Crimp reversibility of boiled off bilateral acrylic fiber. Left, dry; right, wet.

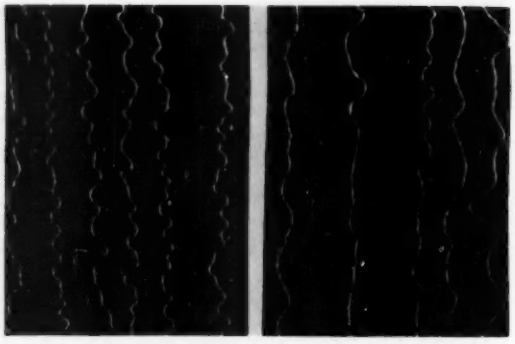

Fig. 8. Elastic recovery of yarn skeins.

A third behavior of the fiber is its response to dyes. The bicomponent Orlon acrylic fiber exhibits generally the dyeing properties of present Orlon. It may be dyed with disperse and with cationic dyes. The brightness and fastness of the dyes are equal to the outstanding level set by Orlon. The primary difference in dyeability is an increased rate of dyeing with cationic dyes. This increased dye rate requires adjustment of dye formulations and procedures specifically for this fiber.

Thus, this bicomponent acrylic fiber is one which gives three-dimensional crimp on heat treatment and then a reversible crimp upon wetting and drying. The effects upon fabric are very significant. The most apparent effect is that of aesthetics. The hand is very wool-like, exhibiting a greater roughness and friction than is noted with conventional acrylic fibers. The wool-like character is quite evident in sweaters and suitings prepared from this fiber.

The second important characteristic imparted by this fiber is fabric elasticity. As can be seen from the stress–strain hysteresis behavior (Figure 8), there is a degree of elasticity imparted by the character of the crimp which is quite unusual. This can be seen in a practical way in a hand-knitting yarn, where elasticity is of vital importance. Another practical demonstration is in sweater bands, where elasticity is essential to performance.

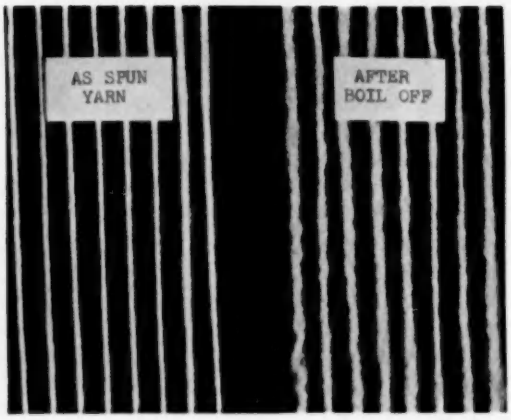

Fig. 9. Spun yarns from bicomponent fiber showing bulk development upon boil-off.

A third characteristic imparted to fabrics by this type of fiber is loft in combination with lightness. It is possible to get high bulk without compacting at the center of the fiber bundle (Figure 9). It is not necessary, then, to use two kinds of fiber—high- and low-shrinkage—to get high bulk. Comparison in knit structures, such as sweaters, indicates the nature of the loft which can be obtained with bilateral fiber in contrast to a conventional homofiber.

The final benefit in fabric form of the bicomponent fiber is somewhat more subtle, but very important. The bicomponent fiber has less of a tendency to compact under heat and pressure, and recovery from hot compacting is rapid when steam is applied to cause the two components of the fiber to swell to different extents. This behavior can be seen from application of the Busse pellet demonstration, in which a fiber mass is compacted under heat and pressure and then treated with steam. Whereas wool bulks up after being pressed and then steamed, conventional acrylic fiber does not recover its bulk. The bicomponent fiber actually fluffs up to the same degree as wool (Figure 10). The same behavior is evident in fabrics which have been exposed to a hot iron and then steamed. Steaming leads to the

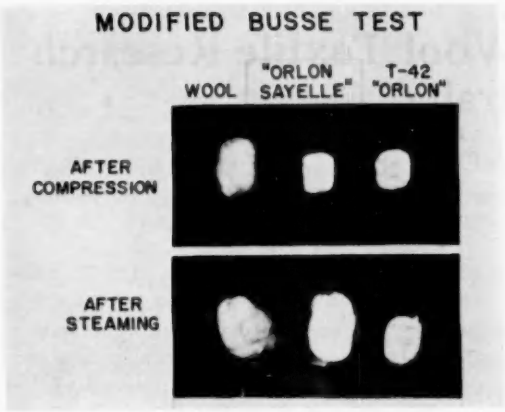

Fig. 10. Recovery of fibers from hot compacting.

recovery of the appearance of the fabrics made from two-component fiber.

It has been possible, through process and equipment development, to bring this bilateral acrylic fiber to the stage of commercial production on a limited basis. Announcement has been made of the trademark, Orlon Sayelle, covering this bicomponent fiber. This trademark replaces the previous designation, Orlon 21 acrylic fiber. The fiber has been introduced initially in styled sweaters and hand-knitting yarns. As additional textile technology is developed for using the fiber and as modifications are made to optimize its performance characteristics, the fiber is expected to find application in wool-like woven and knit structures generally. It is recognized that adjusting differential morphology provides the means for accomplishing these modifications of the present two-component product.

The bicomponent acrylic fiber represents a basically new kind of acrylic fiber, rather than a replacement for present acrylics. It combines the aesthetics and performance of Orlon with the liveliness and behavior of wool. It might be considered to represent to conventional Orlon acrylic fiber the type of premium properties which Merino and mohair represent to wool. It does not abridge the excellent aesthetics and performance of present Orlon in areas for which that fiber was developed.

In summary, a new acrylic fiber having a bilateral or two-component structure has been described. This product shows fiber characteristics of development of three-dimensional crimp when heated and reversible crimping upon wetting and drying. The fiber properties reflect themselves in fabric as wool-like aesthetics, elasticity, loft, and resistance to permanent heat deformation.

Acknowledgment

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Some Developments in Wool Textile Research in Australia[1]

M. Lipson

C.S.I.R.O., Division of Textile Industry, Wool Research Laboratories, Geelong, Australia

Introduction

The past ten years have witnessed a rapid growth of textile research in Australia. Prior to that, research had been mainly on problems of wool production, with little attention to the subsequent processing of the fleece. In 1945, Government and woolgrower leaders wisely provided for continued research not only in wool production but also in utilization. As a result, the Commonwealth Scientific and Industrial Research Organisation (C.S.I.R.O.) was able to enter the field of wool textile research and expand activities so that this financial year about $1 million will be thus spent. Most of these funds are used by the Wool Research Laboratories, consisting of the Division of Protein Chemistry, Melbourne; the Division of Textile Physics, Sydney; and the Division of Textile Industry, Geelong.

It is the purpose of this paper to outline some of the results of direct textile interest which have emerged in the past ten years. In developing the textile research program, emphasis has been placed on problems peculiar to wool, such as impurities like brands and burr in the raw material, the need for scouring, mill operations such as worsted carding and combing, and fabric effects such as anti-moth and shrink-resistant finishes. This by no means represents the over-all research program, which covers a large field of basic chemical and physical studies in addition to the technological problems now discussed.

Sheep Branding Fluids

A serious problem over the years has been the use of sheep-marking materials which are not removed in the normal processing of the wool. A conservative estimate made some years ago of the loss to industry due to the presence of unscourable brands in the Australian clip was over $3 million annually [15]. One of the first projects in the research program was the development of branding fluids for sheep which are removed in normal processing. This research had been initiated in 1943 prior to the setting up of the Wool Research Laboratories, but was intensified after their establishment [14]. In 1950 a formula of a branding fluid was released for commercial use which extensive laboratory and field trials had shown to be satisfactory. This consisted of an oil-in-water emulsion of lanolin, stearic acid, and rosin with appropriate pigments using ammonium soaps as emulsifier. The fluid proved satisfactory in the field except for the one minor disadvantage that several hours were required for it to dry out on the sheep; otherwise it could run during rainfall. Further research resulted in the development of a product free from this defect. This is a water-in-oil emulsion known as Si-Ro-Mark branding fluid, which is now extensively used in Australia. It is manufactured by all the major producers of branding fluid; C.S.I.R.O. licenses approved firms to use its trade mark Si-Ro-Mark. Since release of the formula four years ago, over ½ million gallons of commercial fluid have been produced. Si-Ro-Mark brands will in most cases be completely eliminated from the wool during initial scouring. In some instances, where heavy application has taken place, a small quantity of residual material may remain after scouring, but this is easily removed in subsequent normal processing such as backwashing or hank or piece scouring. The use of Si-Ro-Mark branding fluid by Australian wool growers has practically eliminated the problem of tar from the Australian clip. In a few instances, field performance of the fluid is not entirely satisfactory; experiments are in progress with minor modifications to overcome this slight defect. However, the major factor of removability during processing is our foremost consideration, and in no circumstance are we prepared to sacrifice this qual-

[1] Presented at the 30th Annual Meeting of Textile Research Institute, New York City, March 25, 1960.

ity, even slightly, to obtain an advantage in better field performance.

Solvent Degreasing

A major activity has been the development of a practical solvent degreasing process for wool. As a result of this work, a method has been devised and operated commercially in Australia for several years, during which over 20 million pounds of tops have been produced from solvent-degreased wool. Recently, the process has been further improved and a modified pilot plant constructed in which the wool is carried through solvent jets by means of rotating porous drum conveyers. There are two solvent stages, the wool being squeezed after each stage. After solvent extraction, the wool passes to two cold water stages of treatment and is finally dried. The plant in its earlier form has been previously described by Sinclair [22]. The modified unit is considerably shorter. Total length of the extractor section in the new pilot plant is only 10 ft. This modified unit is capable of processing up to 600 lb. greasy wool per hr. in a 2-ft. width.

Solvent recovery takes place by vacuum distillation after the solvent has been centrifuged to remove dirt. The water stage collects solvent from the wool as emulsion which is split by the centrifuge and the solvent recovered. The only effluent from the plant is the aqueous discharge from the centrifuge which contains some potash salts from the suint of the fleece.

Much experience has now been gained in mill processing of solvent-degreased wool under a wide range of conditions. There are considerable advantages with wool cleaned in this way, as less felting occurs than in the normal scouring operation. Consequently there is scope for simpler early processing, as less carding is needed to open the clean wool.

Solvent-degreased wool can be carded at greater production rates than normally scoured wool. It has also been found to give tops of higher fiber length, neutral in reaction, with better color and less nep than soap-scoured wool. In combing trials under identical conditions, solvent-degreased wool has given as much as 25% less noil than similar wool normally scoured [19]. There is also considerable evidence to show that the solvent process gives higher yields of wool than alkaline scouring [19, 27].

Wool from the solvent plant may not look as attractive to a merchant due to the fact that the staples are preserved and there may be a small amount of "tip" still remaining. However, mill performance and final product leave little doubt as to the advantages of the method. Judgment of scoured wool by appearance instead of performance can be misleading. Thus we were asked recently by a scourer, who was producing an improved product, for a way in which he could mat his wool slightly, as it was more acceptable to certain buyers in the semifelted state!

Solvent degreasing will probably have greatest application in the worsted industry, where it can offer advantages of increased production rates, better combing tears, and an improved top. On the woolen system, increased yields and better final color have been observed in trials so far carried out, but more experiments will need to be undertaken.

Research on carbonizing at Melbourne has led to a simple method for preserving the fiber strength and cutting losses. Resulting from fundamental studies in protein chemistry, it has been found that acid damage to the fiber can be greatly reduced by introducing certain surface active agents into the sulfuric acid used in carbonizing. Most Australian carbonizers now add small quantities of nonionic surfactants to their liquors, with greatly improved results [1].

Shrinkproofing

Methods for reducing the felting properties of wool are being studied along two major lines—first, the application of synthetic resins and natural polymers to wool and second, chemical methods, mainly oxidative.

The resin treatments first led to a process based on the use of N-substituted nylon derivatives applied to wool from alcohol solutions [12]. These were hydrolyzed to the unsubstituted polymer by treatment with acid after resin impregnation. It was found in this work that the treatment was much more effective with smaller quantities of resin if the surface of the fibers were cleaned by alcohol extraction prior to treatment [9]. These findings were also found applicable to other polymer treatments, from which it would appear that a certain amount of foreign material must be removed from the cuticle in order that the resin can be firmly bonded in appropriate sites to individual fibers [9]. Treatment with N-substituted nylon was applied commercially

to hosiery with effective results. It was found in commercial operation that the addition of a small amount of alkali to the alcoholic polymer solution precluded the need for pretreatment [3]. A major difficulty was the use of a solvent of low flash point such as alcohol together with the high cost of treatment, and the method was not extensively applied. A search for water-soluble high molecular compounds resulted in treatments using casein followed by a cross-linking with formaldehyde [10, 11]. Again, it was found that pretreatment of the wool with alcohol was a necessary step in order to obtain satisfactory results with small quantities of polymer without seriously altering the handle of the wool. This method was not extended beyond the laboratory stage.

In the meantime, research continued on the use of chemical treatments to modify scale structure. It was found possible to shrinkproof from aqueous solutions of caustic soda in saturated salt, which inhibited attack on the fiber by the alkali [20]. These observations were extended to the action of oxidizing agents on wool from saturated salt solutions [21]. In the present studies, potassium permanganate has been found the most suitable oxidizing agent. Treatment is carried out using approximately 5% of permanganate on the weight of wool and treating from a saturated solution of salt in standard equipment [2]. The initial commercial application has been in treating woven material such as blankets and shirtings, but more recently the treatment has been extended to wool in other forms. Trials have been carried out on tops, hanks, and knitwear, using standard equipment with satisfactory results. For tops, pressure type machines have proved suitable, and recent tests continuously treating in a backwash have also given good results. It is likely that this method will have wide application in the near future. A major advantage is that there is no effect on handle and no need for any softening aftertreatment. Chemical control during treatment is reduced to a minimum; the reaction can be followed visually by exhaustion of the pink color from the permanganate solution. The salt is kept in a standing bath and reused for economy. In this way, it is possible to produce very economic results. Preferred materials of construction for equipment are fiber glass bonded with resin to steel or wood. The standing bath of salt has been kept in a resin-coated mild steel container.

Mothproofing

Experiments with Dieldrin emulsions have shown that it is possible to mothproof wool with results fast to drycleaning and washing. Initial tests showed that Dieldrin applied to wool from an organic solvent is not fast to drycleaning, whereas when application is from emulsion, the result is fast to drycleaning [16]. This is because the aqueous emulsion treatment causes a certain amount of fiber swelling, which permits some of the compound to enter the fiber [17]. This is difficult to remove completely, and the small quantities remaining are sufficient to protect the wool under practical conditions. The recommended quantity of Dieldrin is 0.05% on the weight of wool, which is considerably in excess of the minimum quantity required. Washing and drycleaning slowly remove some of the Dieldrin, but sufficient is retained by the fiber to protect the garment in normal use. This method is now widely applied in many countries and offers a convenient and economic procedure for protecting wool from insect attack.

Permanent Pleating and Creasing

As a result of fundamental studies on the setting of single wool fibers [4], a method was devised just over two years ago which can produce permanent creases and pleats in garments made from wool. This method has become known as the Si-Ro-Set process and consists of spraying the garments with a solution of ammonium thioglycollate containing a wetting agent just before final pressing in the case of trousers and steaming in the case of pleated skirts.

Treated garments have now come into regular production on the Australian market, where about two million pairs of trousers have been treated, and practically all major skirt pleaters now use the process. Treatment has no effect on the handle or wearing properties of the wool. In most cases, there is no alteration in color, but all shades to be treated should be tested in advance, as some dyes can be affected, particularly under steaming conditions required for pleating.

Dyeing

Research has been undertaken on dyeing and printing along several different lines. Work at the Division of Physics, Sydney, has been concerned with increased absorption of dyes by wool resulting from exposure to ultraviolet radiation [23]. Two-

toned dyeing effects in fabric have been obtained in this way during piece-dyeing. Work of a more fundamental nature at the Division of Protein Chemistry has been concerned with the absorption of dyes from solutions in formic acid [13]. The basis of a rapid dyeing method has been established and experiments are now in progress to ascertain whether a practical and economic method can be worked out. One of the major problems is recovery of the organic acid, which will need to be in high percentages and at low cost for satisfactory economic results.

The melange or vigoureaux printing process has been studied at Geelong; by inclusion of a solvent such as benzyl alcohol in the printing paste, it has been possible to simplify the process considerably [3a]. Shorter steaming times are required, simpler mixtures are used in the paste, and a greater color intensity results for a given quantity of dye. This method is now in commercial operation.

Washable Non-Iron Finish

In the past two years considerable effort has been put into developing washable non-iron effects in pure wool fabric. This has resulted in a process which is now being applied commercially in Australia. Two basic procedures are involved. The wool must be rendered non-felting, and a setting treatment is required to prevent surface puckering during washing [5]. The permanganate-salt method mentioned earlier is used as the shrinkproofing treatment; this is followed by steam setting in the presence of sodium bisulfite to give the non-iron effect. It has been found essential for satisfactory results to dry the cloth free from tensions so as to minimize relaxation shrinkage [6]. As with all fibers, a wash non-iron effect in the fabric means that the final garment can be washed without ironing only when adequate making-up precautions are taken with sewing threads and lining materials. At this stage, we prefer treated fabric to be used in unlined simple garments such as shirts, blouses and skirts, and materials such as curtains, where effects due to sewing threads and linings are minimized. Satisfactory garments have been produced in this way and subjected to extensive wearing and washing trials with good results. It has been found that the material responds very well to machine washing followed by tumble drying and can also be washed and allowed to drip dry. In the latter case, drying is to a large extent evaporative, but due to the high regain of wool, it is not necessary for the fabric to dry below about 25% regain in order to be wearable. Light-weight wool garments will thus dry under normal conditions at a convenient rate for most practical purposes; treatment in itself does not alter the moisture absorption properties of the wool.

The technique should open a field of wool use which could be quite extensive. However, it will be necessary for correct making-up procedures to be adopted if the process is to give its full benefits to the consumer.

Pilling in Knitwear

Recently research has been undertaken to eliminate pilling in certain types of wool knitwear. Although this problem is not as serious with wool as with synthetics, on the other hand it can cause trouble, particularly in better quality articles, and a convenient method of overcoming it would be desirable. This work has shown that certain of the chemical shrinkproofing processes will considerably reduce pilling in knitwear. Some years ago this effect was indicated during shrinkproofing studies with alcoholic alkali [7]. Extending these observations, it has been revealed that certain other chemical shrinkproofing treatments can do likewise. The reason is no doubt through reduced fiber migration as a result of treatment. The permanganate-salt treatment mentioned above is most effective in this regard. In initial tests, results were improved by application of a small amount of polyethylene from emulsion as an aftertreatment. Thus permanganate-salt shrinkproofing followed by a final rinse in polyethylene emulsion to leave about 0.5% of polymer on the weight of wool has reduced pilling in knitwear to almost zero in a standard test used in this work [18]. However, it would appear that there is little practical advantage in the polyethylene aftertreatment, and the shrinkproofing on its own is sufficient. Treated garments have been tested in wearing trials under severe conditions with completely satisfactory results.

Worsted Carding and Combing

A thorough study which is closely linked with research on solvent degreasing mentioned earlier is being made of the preliminary processes in worsted manufacture. In worsted carding, particular attention is being given to the effects of variables such as regain, fiber lubricants, feed rate, and cylinder

speed on amount of waste and product quality. It appears possible to reduce waste considerably by using limited quantities of certain lubricants [8]. This research is still in progress, but results to date indicate that considerable improvements may be possible with existing machinery. Research is also in progress on alternatives to worsted carding [25].

A thorough study is being made of the performance of the Noble comb. In the course of this work it was observed that comb production rates fluctuated tremendously during normal operation of the machine, even with careful attention by skilled operators. This has led to the development of a comb control unit which automatically corrects fluctuations in setover while the machine is in operation [24]. The equipment measures the thickness of the outgoing sliver and uses an electrical servo unit to control the settings of the feed knives. The operator simply sets a dial on the unit at whatever production rate is required and the machine will maintain this rate from beginning to end of a single run and from day to day. It has been found that variations of the order of 30% in output can be reduced to about 3% by installing the comb control unit. These units are in commercial production in Australia, where an initial batch of 24 units has been running for the past year in the major worsted mills. Performance under practical conditions has been most satisfactory, and larger quantities are now being produced for further installation.

Other studies on the Noble comb at present in progress include the effect of factors such as regain, punch sliver weight, lubricants, and temperature on combing tear and quality of the top [26].

Conclusion

The subjects discussed here represent a proportion only of the total research effort. However, they should serve to show that Australia as a wool producer is now keenly interested in utilization research and is actively tackling many of the major problems.

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Recent Improvements in Textile Processing Machinery and Methods[1]

R. A. Rusca

Southern Regional Research Laboratory,[2] New Orleans, Louisiana

Introduction

An important part of the research program of the U. S. Department of Agriculture to increase the utilization of cotton is the development of new and improved textile processing equipment and methods to raise the quality and lower the cost of cotton products. The Department's machinery research, and much of its processing research, is centered at the Southern Regional Research Laboratory, New Orleans. Both fundamental and applied studies are conducted. A large part of the research is concerned with investigating the effect of fiber properties on textile processing and with the development of improved textile equipment for cleaning and carding cotton. This paper will report some of the Laboratory's more recent accomplishments in these fields and will discuss future research needs.

Processing Research

Extensive investigations are being conducted to relate cotton fiber properties to textile product quality and processing efficiency. Among the more important areas of work are blending fibers of contrasting fiber properties, effects of short fibers, effect of fiber properties and processing variables on spinning and weaving efficiencies, and effect of fiber maturity on fabric dimension during weaving and chemical finishing. Following are some recent findings that may be helpful to the industry.

Blending

The blending of immature and mature cottons was investigated to determine if immature cottons can be used to produce acceptable textile products [5]. The results demonstrated that blending cottons of low and high micronaire readings in proportions of 60% and 40% respectively does not detrimentally affect the important physical properties of yarns, or of gray, bleached, and bleached and dyed Type 128 sheeting. Commercial acceptability evaluations showed that, in general, marketable bleached materials can be manufactured from a blend of cotton fibers of extremes in maturity but that the dyed fabrics tended to show excessive neppiness. The findings indicate that properly blended immature and mature cotton fibers can be used to produce satisfactory sheeting and lead to the belief that the inadequacy of present-day blending systems in the cotton textile industry may be one reason for the opinion that immature and mature fibers cannot be blended satisfactorily except within restricted ranges and proportions.

Short Fibers

The influence of cotton fibers shorter than $\frac{3}{4}$ in. on textile product quality and processing efficiency is being studied, using a range in short fiber content varying from 1% to about 20% [27]. Results from these evaluations reveal that:

1. The twist required to obtain maximum yarn strength is not affected by short fiber content.
2. Each 1% increase in short fibers reduces maximum yarn strength by about 1.25%.
3. Increases in short fibers degrade yarn uniformity and particularly yarn appearance.
4. Spinning end breakage rate is related nonlinearly to short fiber content. For a 40/1 (15 tex) filling twist yarn, as short fiber content reaches 14% spinning becomes impractical due to a prohibitively high end breakage rate; for a 30/1 (20 tex) warp twist yarn an increase of short fiber content from 8% to 14% more than doubles the end breakage rate.
5. Fabric (80 × 80 print cloth) appearance and properties are adversely affected as short fibers increase.

In summation, it appears that short fibers are detrimental to both product quality and processing efficiency.

[1] Presented at the 30th Annual Meeting of Textile Research Institute, New York City, March 25, 1960.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

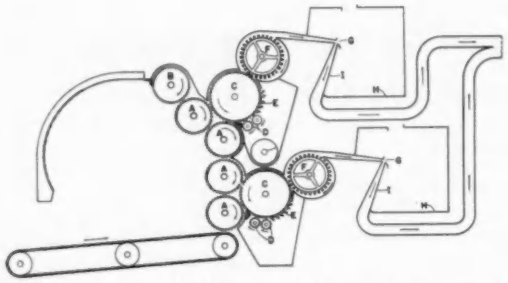

Fig. 1. Schematic diagram of Opener-Cleaner with Aerodynamic Cleaning Attachment.

Machinery Research

In the field of textile equipment, earlier developments by the Laboratory include the SRRL Loom Attachment [12, 15], a device that facilitates the production of high-density and hard-to-weave cotton fabrics, and the widely used SRRL Cotton Opener [23, 24], a machine for improved opening and blending of fibers.

Integrated Cleaning System

Several years ago, research was initiated to develop a system for cleaning cotton at the mills wherein the function of each machine in the system is integrated and synchronized with every other machine [20]. By this approach it was believed that more effective cleaning could be achieved without fiber damage. The proposed system evolved to the present concept of a Bale-Breaker-Blender that opens and blends cotton in any desired proportion from up to 40 bales, an Opener-Cleaner with an integral Aerodynamic Cleaner that provides an over-all trash removal efficiency of 35–45% at 1,500 lb./hr. production, and a Carding Cleaner type finisher picker that removes 50% of the remaining trash at 400 lb./hr. production. The Bale-Breaker is under development; the latter two machines are available commercially and will be discussed briefly.

Opener-Cleaner

The SRRL Opener-Cleaner [22, 25] is the well known SRRL Opener, with built-in cleaning mechanisms. The Cleaner retains the opening and blending ability of the Opener and, in addition, subjects the cotton to cleaning while the cotton is in a very open condition. Figure 1 is a diagram of the Opener-Cleaner equipped with the new SRRL Aerodynamic Cleaner [13]. The machine has four wire-wound processing cylinders (A) with special forwardly inclined teeth, and one cylinder (B) with rearwardly-inclined teeth. Cylinders (C) remove the small tufts of loosely held cotton from cylinders (A) and clean the cotton by means of a pair of combing cylinders (D) used in combination with textile-type grid bars (E) applied in an unconventional manner.

The doffing system utilizes soft revolving strip brushes (F) which remove the cotton from the cleaning cylinders and at the same time serve as centrifugal fans [14]. The process of doffing the cotton from the cleaning cylinders results in further opening and loosening of the trash. The cotton is carried by air currents through specially shaped ducts that spread out the cotton into a wide, thin sheet. At point (G) the cotton changes direction abruptly under the influence of suction from a conventional condenser; motes and trash are ejected into waste box (H) while the cotton goes into ducts (I) and then to the condenser.

Evaluations of the Opener-Cleaner without the aerodynamic attachment indicate that the machine removes an average of about one-third of the trash in cotton, depending upon the type of cotton and trash, at a production rate of 1,500 lb./hr. (Table I). These results are confirmed by mill experience.

Addition of the air-type cleaner increases the over-all cleaning efficiency of the machine by about one-third without increasing the percentage of fiber in the waste. Mill evaluations of the combined Opener-Cleaner Aerodynamic Cleaner are not yet available due to the recency of this development.

Carding-Cleaner Picker

The final unit in the cleaning system is the SRRL Carding-Cleaner [8, 9]. Designed as a modification

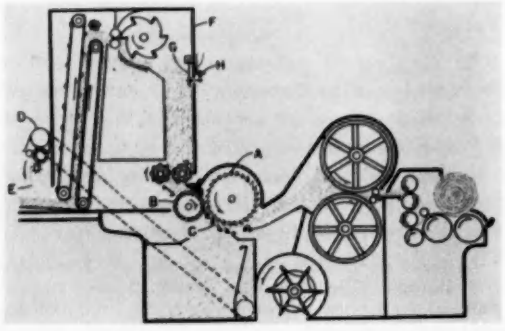

Fig. 2. Schematic diagram of Carding Cleaner Picker.

for standard cotton textile pickers, this development increases the cleaning efficiency of the picker about 400%. A schematic diagram of the machine is shown in Figure 2.

Essentially, the picker conversion consists of replacing the blade or Kirschner beater with a wire-wound cylinder (A). The pedal evener motion is replaced with a wire-wound "antipluck" feed roll (B). The feed roll is unique in that the wire is wound into two spiral grooves so that the teeth in one groove point in the opposite direction to the teeth in the other groove. The forwardly-inclined teeth advance the cotton from the blending reserve delivery to the carding-beater cylinder. As the carding-beater strips the feed roll, the cotton is combed across the backwardly-inclined teeth and is thoroughly opened. The cotton is then cleaned by a set of four triangular grid bars (C). Lint loss through the grids is minimized by a simple lint recovery system (D) which draws a slight stream of air across the top of the trash box to catch the falling fibers. The recovered fibers are deposited on the incoming cotton (E) for reprocessing, or the fibers may be collected separately.

Two changes are made to improve the feed system. The belt-shifting mechanism controlling the feed to the blending reserve (F) is replaced with a fast-acting pneumatic clutch [10] and the rake-type control in the blending chute is replaced with a light aluminum gate (G) directly coupled to a mercury switch (H).

Pilot-scale evaluations of the Carding-Cleaner installed in a one-process two-beater picker were conducted in comparison with a relatively short opening line composed of two spiked cylinder cleaners in tandem, porcupine cleaner, and a two-section picker. The tests reveal no difference in fiber length distribution or tensile strength of cotton from laps produced by the two lines. As shown in Table II, the Carding-Cleaner line removes 52.6% of the trash, whereas the control line removes 32.9%. Waste from the control line contains twice as much lint as the experimental line.

The cleaning efficiency of the Carding-Cleaner alone is presented in Table III. This stage takes out an average of 45% of the trash remaining in the cotton after the cotton has been processed through the hopper, breaker-picker, and blending reserve.

TABLE I. Effect of Opener-Cleaner on Cleaning Efficiency and Waste *

Quality of cotton	Cleaning efficiency, %	Waste removed, %	Trash in waste,† %	Fiber in waste, %
M grassy, 1 1/16 in.	23.8	0.94	76.7	23.3
M, 1 1/4 in.	31.7	1.11	85.9	14.1
LM, 1 1/8 in.	25.0	2.13	89.4	10.6
LM, 1 1/32 in.	34.1	2.19	85.2	14.8
SGO, 3/4 in.	37.9	4.22	88.4	11.6
SGO, 1 1/32 in.	43.2	4.37	88.1	11.9

$$\text{Cleaning efficiency} = \frac{\text{trash in cotton fed} - \text{trash in cotton delivered}}{\text{trash in cotton fed}}$$

* Determined with a Shirley Analyzer.
† Includes invisible loss.

TABLE II. Effect of the Carding Cleaner Line on Waste Removal

Processing line	Cleaning efficiency* %	Waste removed, %	Lint in waste,* %	Lap production rate, lb./hr.
Acala 4–42, SLM, 1 1/16 in., 74% maturity (NaOH), 3.9 Micronaire reading				
Control	33.1	1.91	42.6	375
Card. Clr.	53.5	1.87	16.8	321
Paymaster, SLM, 31/32 in., 91% maturity (NaOH), 4.9 Micronaire reading				
Control	19.1	1.27	40.6	381
Card. Clr.	45.3	1.25	20.4	314
Deltapine 15, LM, 1 1/16 in., 81% maturity (NaOH), 4.3 Micronaire reading				
Control	46.4	2.87	28.0	381
Card. Clr.	59.1	2.50	17.8	322
Average				
Control	32.9	2.03	37.1	379
Card. Clr.	52.6	1.87	18.3	319

* Determined with a Shirley Analyzer.

TABLE III. Waste Removal by the Carding Cleaner Unit

Variety of cotton	Cleaning efficiency,* %	Waste removed, %	Lint in waste,* %
Acala 4–42	45.2	1.18	9.8
Paymaster	39.5	0.77	11.4
Deltapine 15	49.9	1.44	13.1
Average	44.9	1.13	11.4

* Determined with a Shirley Analyzer.

Card waste and nep count are slightly lower on cotton from the Carding-Cleaner line. The effect of the two lines on yarn properties is shown in Table IV. There are no significant differences in strength, uniformity, or grade.

Uster Lap Varimeter [3] measurements on laps from the Carding-Cleaner line range from 3.1% to 3.6% uniformity. These values fall between Uster standards of 3.6% U for "average" and 2.4% U for "even." Carding-Cleaner laps are highly felted and free from lumps.

Evaluation of the Opener-Cleaner, Carding-Cleaner integrated system with a limited number of cottons indicates that the two machines will remove from 70% to 80% of the foreign matter. The waste averages about 85% trash and 15% fiber, with approximately 60% of this fiber being shorter than ½ in. in length.

Granular Card

Concurrent with research on cleaning equipment, investigations were conducted to improve the quality of sliver and reduce the waste from the cotton textile card. Extensive aerodynamic studies [17] revealed that carding is accomplished through mechanical action and not through air action. Further studies led to the conclusion that the essential requirement for carding is that the tufts and unopened groups of fibers deposited on the cylinder by the lickerin encounter a resistant force sufficient to separate and spread the fibers over the entire area of the cylinder surface before reaching the doffer. Based on these principles, the SRRL Granular Card was developed [16, 21].

The Granular Card is a standard flat top card converted to carding without flats. The flat assembly and flexible bends are replaced with an air-tight cover with an aluminum oxide carding surface closely spaced to the main cylinder, and a small metallic wire roll is installed in conjunction with the lickerin to preopen the fiber tufts thoroughly before carding. Although not required for carding without flats, the use of a modified lickerin cover that improves cleaning at the mote knives is recommended.

The general design of the Granular Card is shown in Figure 3, wherein lap (A) is fed under the new-type lickerin cover (B) to the lickerin (C) which deposits the fibers on main cylinder (D) in the conventional manner. Large tufts or groups of fibers are combed from the main cylinder by preopener roll (E), which returns these tufts to the lickerin for reprocessing. The fibers on the cylinder (D) are subjected to a carding action by the granular surface (G) on the underside of stationary cover (F). Doffing is accomplished by the usual doffer cylinder (H) and comb mechanism.

[3] Mention of trade names and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

TABLE IV. Effect of the Carding Cleaner Line on Yarn Properties

Processing line	Single strand: Yarn no. × brk. load, oz.	Single strand: elongation, %	Skein: Yarn no. × brk. load, lb.	Uniformity*: @ 8 yd./min., CV%	Uniformity*: @ 50 yd./min., CV%	Grade
			Acala 4–42, 28/1 (21.1 Tex) yarn			
Control	309	6.7	2493	19.3	19.5	C+
Card. Clr.	321	6.8	2481	20.0	20.2	C+
			Paymaster, 22/1 (26.8 Tex) yarn			
Control	282	7.0	2275	18.8	18.9	C+
Card. Clr.	281	6.9	2272	18.7	18.8	C+
			Deltapine 15, 28/1 (39.4 Tex) yarn			
Control	275	6.9	2218	20.5	21.3	C+
Card. Clr.	276	7.0	2240	19.9	20.2	C
			Average			
Control	289	6.9	2329	19.5	19.9	C+
Card. Clr.	293	6.9	2331	19.3	19.4	C+

* Determined with an Uster Yarn Evenness Tester.

Technical details of the Granular Card were made available to the textile industry in April 1959. To date, 22 textile machinery manufacturers are licensed under USDA patents to produce the card, and about 65 mills have experimental installations of one to five cards. Figure 4 is a photograph of a Granular Card in a cotton mill, and Tables V and VI present mill results [2].

This new method of carding should lower processing costs. The customary 2–3% flat waste is eliminated, dust and fly are practically eliminated, card weight is reduced about 800 lb., power requirement is reduced by ½ hp, and product quality remains about the same. There is a slight decrease in neps in the web and the possibility of a slight decrease in yarn appearance grade.

Future Research

Need

Cotton textile processing equipment has advanced a long way in the past 50 years; cleaning and carding machines such as described above, high-speed drawing, long-draft roving and spinning, large packages, high-speed warping and slashing, shuttleless looms—in fact, practically all steps in mill processing equipment—have benefited from major improvements. But despite outstanding improvements in individual machines, textiles are still produced by a system based on the use of discontinuous, multistage processing steps. The modern cotton mill utilizes as many as 15 processing stages and, compared with manufacturing systems for paper [19] and other competitive products, an excessive amount of labor.

Some research workers believe that textile proc-

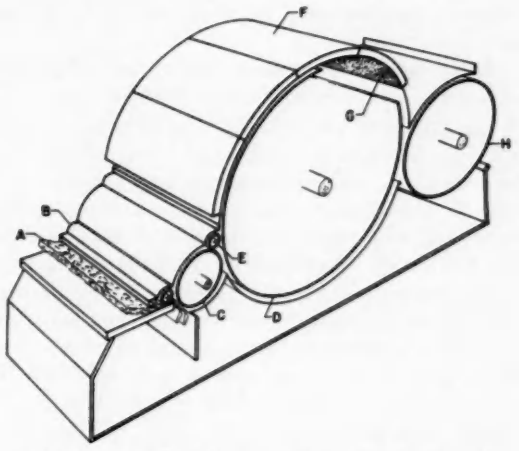

Fig. 3. Pictorial diagram of the Granular Card.

TABLE V. Comparison of Granular Card and Fillet Wire Flat Card *

	Granular card	Flat card
Sliver delivered (calc.), %	97.31	95.06
Motes and fly, %	1.72	1.25
C and D strips, %	0.97	0.86
Flat strips, %	0.00	2.82
Neps/100 sq. in.	9.2	10.3
Yarn number	31.6 (19.3 Tex)	30.3 (19.5 Tex)
Skein break constant, lb.	2117	2060
Uster yarn variation, %	15.4	15.9
Yarn appearance grade	B−	B+

* Data courtesy of Avondale Mills.

TABLE VI. Comparison of Granular Card and Metallic Wire Flat Card *

	Granular card	Flat card
Sliver delivered, %	97.90	96.85
Motes and fly, %	1.81	1.57
Sweeps, %	0.17	0.23
Flat strips, %	0.00	1.23
Invisible loss, %	0.12	0.12
Neps/100 sq. in.	30.9	29.3
Yarn number	14.2 (41.6 Tex)	14.5 (40.7 Tex)
Skein break constant, lb.	1960	1900
Uster yarn variation, %	16.0	16.0

* Data courtesy of Avondale Mills.

essing equipment has reached the point where large increases in quality and reductions in manufacturing costs are not likely to be accomplished by modifications of equipment or even by the development of radically new machines that must fit into the existing systems [4]. Although much technological progress has been made, the traditional approach of improving individual machines rather than the processing system as a whole has proved a handicap in attempts to drastically increase quality or reduce processing costs.

It has long been the conviction of the author that substantial increases in the utilization of cotton can be accomplished through the development of radically new methods for producing cotton textiles. He believes that a comprehensive research program can lead to revolutionary changes in processing equipment that will materially enhance product quality and will reduce manufacturing costs by one-half.

The expenditures for a program of pioneering research of this scope would be large and, as with all research, there can be no guarantee of success. It is apparent, however, that a fresh approach, a break from traditional thinking is needed now. A broad, integrated research program will produce fundamental information that should lead to the development of improved methods of textile processing. The benefits to the industry and the nation that could result from the success of such research are difficult to estimate, but in the United States alone, a reduction of 5% of the $18.5 billion cost to the consumer of cotton textiles [3] would save almost $1 billion annually.

Tools of Research

Scientific knowledge is available which has limited application for modifying standard textile equipment but which has real promise for serving as a basis for a completely new processing system. Much knowledge of aerodynamics has been accumulated since the start of World War II [11, 28]. The possibility of processing cotton into yarn by electrostatic forces has been reported [18] as has electrostatic cleaning and aligning of cotton fibers [6, 7]. The development of powerful sources of ultrasonic energy [1] makes available another potential means for processing cotton. Automation is being used to increase efficiency [26]. These, and other techniques of modern science, provide many new tools that can be utilized in the development of an efficient system for processing textiles.

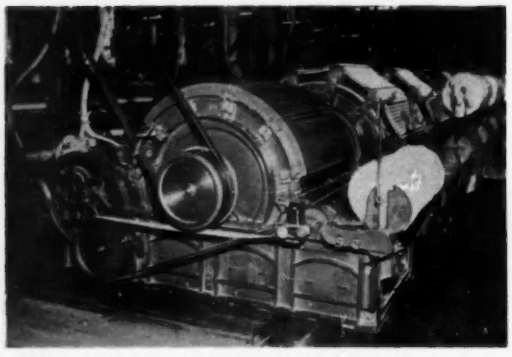

Fig. 4. Photograph of Granular Card in cotton mill.

Plan of Research

The proposed research can be conducted logically and efficiently in two phases, the first being concerned with investigations of a fundamental nature and the second with engineering and development activities. Research conducted under the first phase would involve basic investigations and the development of working principles and experimental laboratory equipment. Consideration should be given to aerodynamic, electrostatic, hydrodynamic, ultrasonic, chemical, and mechanical investigations. Other areas such as electrodynamics and electromechanics could be investigated as the need arises. Upon the successful development of a promising new concept for producing higher quality, lower cost cotton textiles, the second phase would be initiated to develop pilot-scale equipment of adequate size for reliable evaluations of technical performance and economic practicality.

To achieve maximum efficiency in processing cotton fibers, the pertinent physical properties of cotton (e.g., length and length distribution, extensibility, convolution, and coefficient of surface friction) would be utilized as parameters of engineering design. Continuous processing and automation would be incorporated in the system.

The second phase of the research program would be one of machine design and pilot- and mill-scale evaluations, and could be carried out by textile machinery manufacturers or research organizations.

The program envisioned above would probably cover a period of 10–20 years continuous effort and the expenditure of $10–20 million. This is a long and expensive effort; nevertheless it is suggested that the time has come for serious consideration of

the need for, and the advantages of, a scientifically developed, efficient method for converting cotton fibers into high quality textile products. Without doubt the present processing system can and will be continually improved; the question resolves into whether the evolutionary approach followed for the past 200 years is as effective or as rapid as the exciting possibilities of revolutionary changes that might be achieved through concentrated research.

Acknowledgment

The author is pleased to thank L. A. Fiori for preparing the section on processing research, and to acknowledge that the Opener and Opener-Cleaner were developed in association with R. C. Young and the Granular Card in association with A. L. Miller and R. S. Brown. The Carding Cleaner was developed by G. J. Kyame and W. A. Latour and the Aerodynamic Cleaner by M. Mayer and J. I. Kotter. All are members of the staff of the Southern Regional Research Laboratory.

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SM27, A Man-Made High-Modulus Cellulosic Fiber

G. V. Lund and J. Wharton

Courtaulds (Alabama) Inc., Mobile, Alabama

Introduction

RAYON staple as normally available throughout the world is an extremely versatile fiber, as is evidenced by the tremendous weight which is consumed each year. For example, 463 million pounds were consumed in the USA alone during 1959. The great number of advantages of this fiber are, therefore, self evident, and will not be reiterated here.

However, Courtaulds, as does every competent manufacturer, keeps the strengths and weaknesses of its products under constant review, and is well aware that rayon, as all fibers, has its limitations.

What then are the limitations which block the further expansion of rayon in certain directions?

Rayon has a low initial modulus when wet. One of the effects of this is to make continuous finishing processes impossible, in spite of all the potential cost savings, because rayon fabrics are very easily extended when wet. It follows, therefore, that the satisfactory production of fabrics stable to laundering is almost impossible after dyeing on continuous machines.

For the same basic reason, it is not possible to use the Sanforized process on rayon which has not been resin finished, but resin-finished rayon may be Sanforized.

Again for the same reason, the stability of normal commercial fabrics to laundering is dependent on the stability of the resin treatment, a treatment which is under constant cost cutting pressure, which makes for a high percentage of commercial fabrics with less than optimum long-term laundering stability in commercial laundries.

In the course of an investigation of the stability of fabrics made from cellulosic fibers, it was found that the amount of progressive shrinkage of fabrics made from cellulosic fibers was highly dependent upon the Hookean modulus of the fibers when wet [2]. This suggested that a fiber with a Hookean modulus when wet higher than about 0.6 g./den. at 5% extension would not undergo progressive shrinkage in fabric form.

The amount of shrinkage of a fabric from the loom state to a relaxed state is essentially the sum of the shrinkage due to relaxation of the fabric structure [1] and that due to relaxation of fiber strains imposed during processing. The amount of shrinkage of cotton from loom state to relaxed state is considerably less than that of rayon; it was, therefore, reasoned that a reduction of this shrinkage to a value of the same order as that of cotton fabrics would be obtained with fibers of Hookean moduli in the wet state of the same order as that of cotton [3].

One of the advantages of cotton is that, because of its high Hookean modulus, it can be vat dyed on continuous machines, then compressively shrunk; after these inexpensive finishing processes, it is inherently stable. It was reasoned that a regenerated cellulosic fiber with a high Hookean modulus when wet could be finished in the same way, and would, therefore, not be subjected to as much shaving of safety factors as seems inevitable with rayon under the economic conditions prevalent in this country today.

Fine yarn rayon fabrics, which must utilize 1½-den. fiber, feel somewhat limp in hand, a factor which, although an advantage for many fabrics, is a limitation on the use of the fiber during those periods when the market requires a firm hand. In practice a firm hand is obtained by the use of so-called "hand builders," formulations which vary from finishing plant to finishing plant and are usually considered to be secret but which usually consist of condensation products of amino compounds with formaldehyde, of sufficiently high molecular weight to lie on the surface of the fiber, together with acrylic resins and/or converted starches and softeners.

However, in terms of practicality, none of these formulations is to our knowledge stable to repeated laundering; consequently, another of the limitations of rayon when a firm hand is desired is its tendency to lose the stiffness added by the hand builder.

Although the complete interaction of single fiber

[1] Presented at the 30th Annual Meeting of Textile Research Institute, New York City, March 24, 1960.

TABLE I. Tensile Physical Properties of SM27, Fibro, and Cotton

	SM27	Fibro	Cotton
Tenacity, g./den.			
Dry	3.0–3.4	2.5	2–3
Wet	2.1–2.5	1.4	2–3
Elongation at break, %	7	18	5–7
Initial modulus, g./den.	90	50	40
Fiber elastic recovery, %	50	40	50
Stress, wet, at 5% extension, g./den.	1.2	0.1	1.2
Yield point, dry			
Stress, g./den.	1.0	.75	—
Strain, %	1.5	1.5	—

physical properties with fabric hand is not fully understood, it was clear that a fiber with an initial modulus higher than that of rayon at normal relative humidities would be likely to produce, denier for denier, fabrics with a firmer hand, not quite so dependent upon the somewhat unstable properties of hand building formulations.

Rayon swells to a gel of very low physical strength during the dilution phase of mercerization when the effective concentration of caustic soda passes through the region of maximum swelling, that is, from 9% to 12%. This limits the practical use of rayon with cotton, and makes it substantially impossible to utilize the stabilizing effects of mercerization on 100% rayon fabrics.

These considerations led us to re-examine the field of rayon manufacturing technology.

Dr. Shozo Tachikawa [5], a Japanese, has developed a process for producing a cellulosic fiber, Toramomen, which, upon evaluation, seemed to meet our requirements in that it had a high Hookean modulus when wet, a higher Hookean modulus than rayon when dry, and a higher degree of polymerization than normal rayon. Initial evaluation of the fiber showed that it did indeed make stable fabrics with a firm hand and was sufficiently stable to caustic soda solutions to suggest that fabrics made from it could be mercerized. These fibers, in contrast to all other known regenerated cellulose fibers, exhibited a fibrillar structure when swollen in 70% nitric acid.

This then was the clue, and an extensive research program was entered into which resulted in the development of a process by which are manufactured Courtaulds SM27/SC28 fibers. These fibers, although manufactured by a commercially practicable process differing from the Tachikawa process, possess properties very similar to those of the original Toramomen type of fiber.

Fiber Characteristics

Table I shows the tensile physical properties of the fibers. It will be seen that they are stronger than rayon at normal relative humidity, and much stronger when wet.

In Figure 2 are given typical stress–strain curves for the fiber, together with those for rayon and for cotton. These illustrate clearly the effect on tensile properties of the particular type of crystallinity of the fiber.

Figure 3 shows the type of cross section of the fiber, together with that for a normal rayon. The typical crenulated section has been replaced by a round profile.

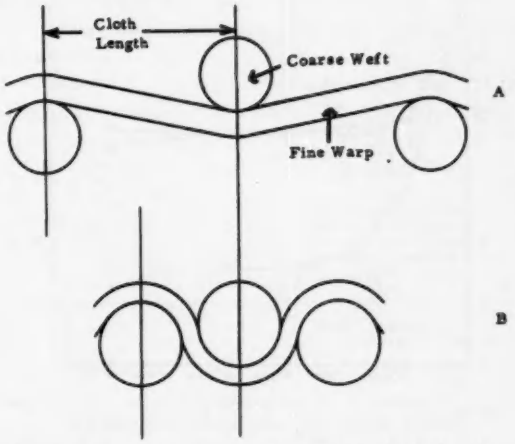

Fig. 1. A geometric explanation of cloth shrinkage (from Collins, "Principles that Govern the Shrinkage of Cotton Goods").

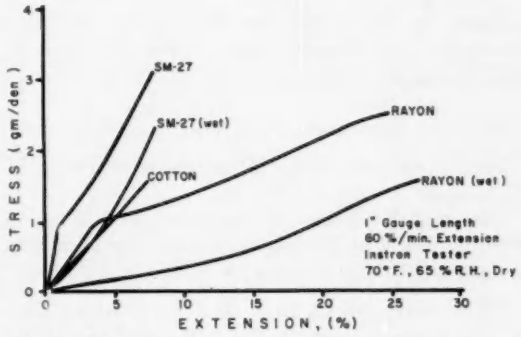

Fig. 2. Stress–strain curves of SM27, Fibro, and cotton.

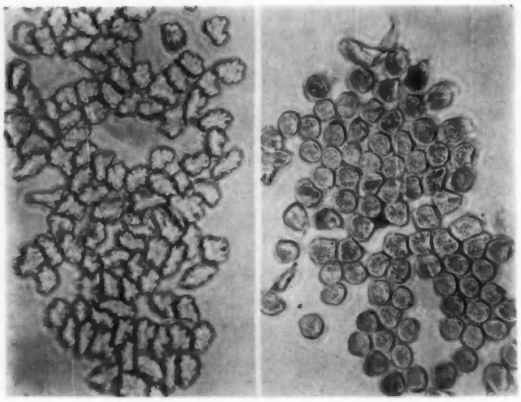

Fig. 3. Cross sections of SM27 (right) and Fibro.

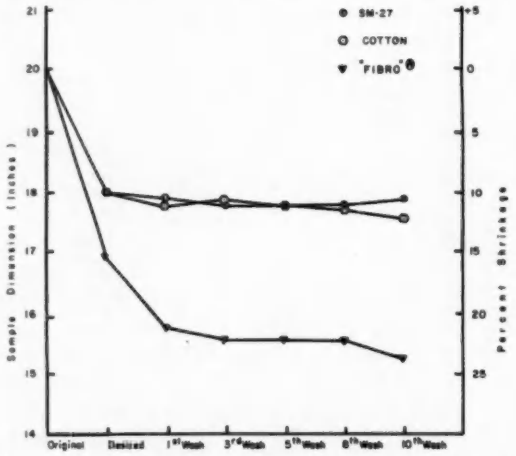

Fig. 4. Comparison of laundering shrinkages of SM27 and cotton (8-lb. load, 140° F., 60 × 40 fabric).

Comparison of Performance with Initial Thought

Shrinkage from Loom State to Relaxed State

Figure 4 shows that the amount of relaxation shrinkage is of the same order as that of cotton in the same fabric construction.

Progressive Shrinkage

Fabrics made from this fiber behave as cotton in this respect.

Possibility of Vat Dyeing on Continuous Machines Followed by Compressive Shrinkage

Plain weave fabrics have been vat dyed on continuous machines and Sanforized treated to 3–5% shrinkage in a boil wash (40 min. at the boil).

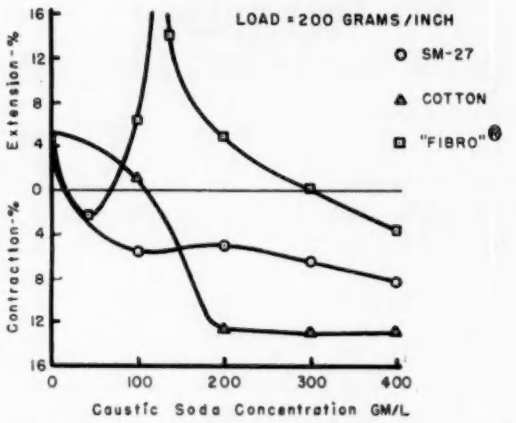

Fig. 5. Length changes of Fibro, SM27, and cotton as a function of caustic soda concentration.

A trial in a tight twist gabardine construction failed, but we are informed that this procedure is very difficult on cotton fabrics of the same construction.

However, progress on this theme is sufficiently encouraging to lead us to believe that large scale continuous vat dyeing of fabrics made from this fiber must be looked for in the future.

Mercerizability

Treatment with caustic soda. The high resistance of the fiber to caustic soda solutions is illustrated by Figure 5, in which the length of a fabric at a load of 200 g./in. of width is plotted against the concentration of caustic soda in which the fabric is suspended. It is clear from this work [4] that SM27 is much more stable in caustic soda solutions than is normal rayon, and a very low strength gel is not formed.

We have successfully treated SM27 fabrics with caustic soda (6–18%) in mercerizing ranges. The luster of the fabrics is increased, without, however, developing a metallic synthetic type of glitter. The well known stabilizing effect of mercerizing is obtained on SM27 just as it is with cotton, so that the amount of shrinkage to be removed compressively is reduced, often by a factor of two. Since treatment with caustic soda sets the fabric in a swollen state [6], the fabric develops a high wet crease angle, with improved drip-dry properties.

Of extreme importance is the fact that the setting effect of caustic soda greatly improves the resistance to raveling of raw seams. The manufacture of

washable garments without protected seams would appear, therefore, to be possible.

A Further Example of the Importance of a High Hookean Modulus When Wet

The so-called elevator effect in draperies is a phenomenon in which the draperies change in length under conditions of changing relative humidity of the atmosphere in which they are hung. All the drapery fabrics examined by us have increased in length with increasing relative humidity. We have not, however, examined any fabrics with a substantially nonextensible warp, such as glass fiber. However, rayon draperies must extend at higher relative humidities because, as the relative humidity increases, the weight per unit area of the fabric increases and simultaneously the Hookean modulus of the load-bearing warp decreases; consequently, the warp and the fabric extend. The extension of the single fibers cannot extend beyond their yield point since, in the draperies examined, the extension at a high relative humidity is recovered as the relative humidity decreases. This behavior may be modified during the first few relative humidity cycles by the stress history of the fabric before hanging.

The dry and wet moduli of SM27 are sufficiently high to reduce this elevator effect in a normal bark cloth drapery construction to less than 1%. This is illustrated by Figure 6.

Other Properties of the Fiber

Yarn Manufacture

It has been found that, in general, machine speeds and settings suitable for rayon are suitable for SM27.

However, since the fiber is stiffer than rayon, it appears, denier for denier, to be easier to break fibers in processing and harder to make neps.

Beating in the opening room should be kept to a minimum, and a licker-in speed of about 200 rpm is recommended, compared with 400 rpm as a normal average speed for viscose rayon.

Drafting programs similar to those used in rayon may be used, the only steps to be taken being those well within mill competence to handle a rather compact sliver.

Conservative spinning limits are 50s for $1\frac{1}{4}$ den. $1\frac{9}{16}$ in. staple, 40s for $1\frac{1}{2}$ den. $1\frac{9}{16}$ in., and 20s for 3 den. 2 in. fiber.

There is a suggestion that the fiber takes more kindly to the relative humidities common in cotton mills than does normal rayon.

Twist factors in the region of 2.8 for $1\frac{1}{4}$ den. $1\frac{9}{16}$ in., 3.0 for $1\frac{1}{2}$ den. $1\frac{9}{16}$ in., and 3.2 for 3 den. 2 in. fiber have been found to be a suitable starting point for experimentation.

Fabric Manufacture

Mills have slashed SM27 warps using both cotton and rayon types of size formulation, both with reasonable weaving efficiency, but work has not yet been undertaken to specify the optimum type of size formulation.

Weaving has been carried out within the range of relative humidity from 60 to 80%; there are indications that the higher relative humidity is better.

The high tensile modulus of the fiber, both wet

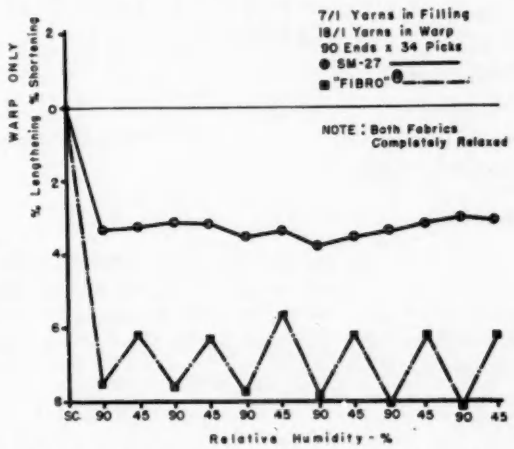

Fig. 6. Elevator effect in Fibro and SM27 bark cloth draperies.

TABLE II. Modification of Wet and Dry Wrinkle Recovery Angles of SM27 Fabrics by Treatment with Caustic Soda

	Challis			Gabardine	
	Control	6% NaOH	18% NaOH	Control	6% NaOH
WRA, °					
Dry	113 × 108	104 × 107	74 × 84	88 × 101	73 × 89
Wet	98 × 80	118 × 101	109 × 125	102 × 65	112 × 124

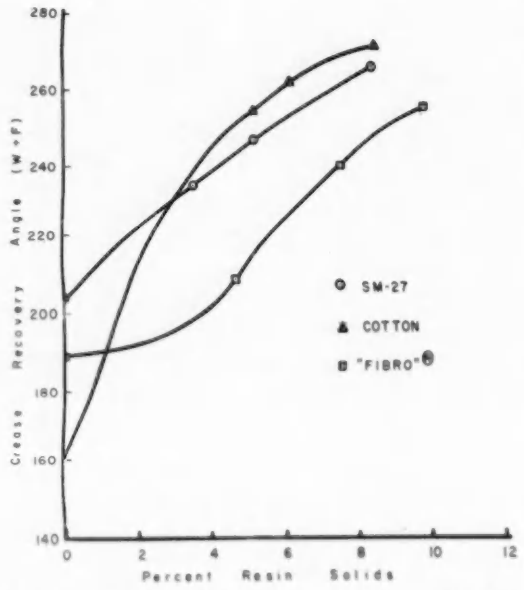

Fig. 7. Wrinkle recovery angle of SM27 and cotton as a function of resin solids (DMEU).

and dry, seems greatly to reduce the danger of sett marks in comparison with normal rayon.

Finishing

Preparation

Normal rayon enzyme desizing operations appear to be suitable, with no necessary deviation from standard practice.

Bleaching

This fiber, in common with all regenerated cellulosic fibers, is easily tendered by bleaching procedures using hydrogen peroxide. However, excellent whites have been obtained by the use of sodium hypochlorite.

Dyeing

In terms of dye affinity, the fiber lies between cotton and normal viscose rayon. Initial indications are that dye formulations give degrees of fastness to light and washing on SM27 similar to their fastness when dyed to the same depth on rayon.

Resin Finishing

One effect of the higher degree of crystallinity of this fiber is to alter radically the relationship between the amount of resin applied and the Monsanto crease angle developed. In this respect, the fiber is more like cotton than like rayon. This effect is illustrated in Figure 7.

The effect of cross-linking on the tensile properties of these fabrics is quite different from the behavior of cotton. In direct contrast to cotton, which suffers major losses of tensile strength on resin treatment, fabrics made from this fiber suffer little or no loss in strength, as shown by Figure 8.

Fabrics made from this fiber, in common with all fabrics made from cellulosic fibers, lose in resistance to abrasion on cross-linking. At the same crease angle, fabrics made from this fiber appear to be slightly inferior to bleached cotton fabrics when dry and slightly superior to them when wet.

The Production of Wash-and-Wear Fabrics from SM27

Combination of treatment with caustic soda on a conventional mercerizing range with cross-linking finishes makes possible the production of fabrics with a high crease angle, wet and dry, and consequently with a good wash-and-wear rating.

The attractive luster and resistance of seams to raveling of fabrics made in this way makes them extremely attractive and practical.

Conclusion

There is no all-purpose fiber. Rayon staple is perhaps the nearest approach to this ideal which is presently available in volume. There can be no stronger evidence of this than the tremendous volume which is used throughout the world in a very wide range of end uses. However, our work suggests that a fiber with most of the advantages of rayon, but with a high Hookean modulus, both dry and wet, and good resistance to caustic soda solutions will be able to enter markets hitherto closed to rayon.

The work here reported shows that SM27

a. exhibits a high Hookean modulus both dry and wet;
b. responds well to caustic soda treatments up to and including mercerizing strength;
c. cross links with conventional resin at add-ons normal to cotton, resulting in good dry wrinkle recovery characteristics with strength retention better than cotton similarly treated;
d. produces fabrics of good stability (compared to rayon or cotton) with no treatment. Upon

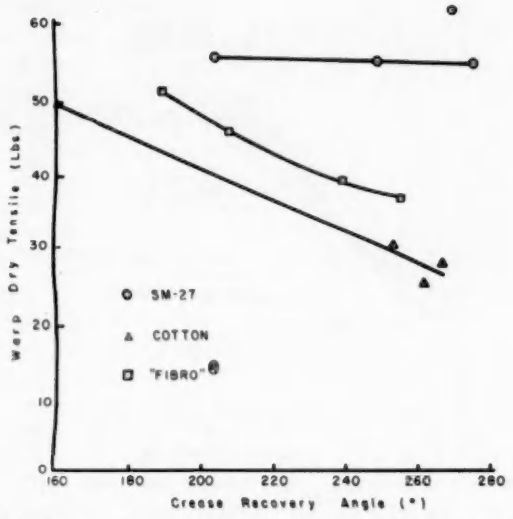

Fig. 8. Tensile strength versus wrinkle recovery angle of resin treated SM27 and cotton (60 × 40 fabric).

resination, with pretreatment with caustic soda, this stability is enhanced with added bonuses of ravel-resistant seams, improved luster, and improved wet and dry wrinkle recovery characteristics.

Further work is indicated in the study of blends of SM27 and other fibers and in the details of finishing techniques.

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The Structure and Properties of Arnel 60—A New Cellulose Triacetate Staple Fiber[1]

B. Sheldon Sprague

Summit Research Laboratories, Celanese Corporation of America, Summit, N. J.

Abstract

A new cellulose triacetate staple fiber, Arnel 60, is undergoing development. This fiber has tensile strength in excess of 2 g./den. and elongation of about 25% which imparts higher strength to spun yarns and permits the spinning and use of much finer counts, since fiber deniers as low as 1.5 can be utilized. The wet and hot wet mechanical properties of Arnel 60 are also improved over Arnel staple, suggesting improved washability and ease-of-care performance. The improvement in mechanical properties is ascribed to increased orientation and a narrower molecular tautness distribution. Unlike Arnel, the fiber has a rough textured surface which provides a natural semidull luster and gives, in conjunction with natural crimp, sufficient cohesiveness for fiber processing. Arnel 60 is similar to Arnel in heat settability, ironing and glazing performance, dimensional stability, dyeing behavior, and dyefastness.

Introduction

The introduction of Arnel[2] cellulose triacetate fiber in late 1954 provided the textile industry with a material having several advantages over secondary cellulose acetate [4]. Such properties as "heat settability," high thermal resistance, excellent dimensional stability, relatively little effect of moisture on mechanical properties, excellent dyefastness, and considerable resistance to saponification have, in addition to the usual filament applications, directed the use of this fiber toward many washable staple fabric applications, both alone and in blends, particularly

[1] Presented at the 30th Annual Meeting of Textile Research Institute, New York City, March 25, 1960.
[2] Reg. U. S. Pat. Off.

with rayon and cotton. However, as is the case with acetate, the limited fiber strength has restricted these staple fiber applications to lower count yarns and heavier fabrics [1, 2, 3, 5].

In order to provide a significantly greater range of applications for triacetate staple, it was deemed desirable to develop a fiber having higher dry tensile rupture characteristics, capable of being spun to deniers as low as 1.5, but retaining all of the desirable characteristics of the existing triacetate, particularly thermal and moisture resistance.

This paper will deal with the structure and properties of such a triacetate fiber, Arnel 60, which is now in an advanced stage of development.

Fiber Structure

In order to preserve the many advantages of Arnel triacetate, it has been necessary to utilize the same polymer for Arnel 60; that is, cellulose triacetate having a combined acetic acid content of about 61.5% and an intrinsic viscosity of 2.0 (as measured on the regenerated cellulose by cupriethylene diamine fluidity). Accordingly, changes in strength and general stress–strain behavior have been brought about by alteration of fiber microstructure rather than by changes in chemical constitution.

Methods for improving the strength of fibers usually involve increasing the molecular orientation, increasing the degree of crystallinity, improving the molecular tautness distribution, or some combination of these factors. The concept of molecular tautness involves the distribution of free chain segment lengths lying between points of intermolecular attraction. Figure 1 shows this schematically. In

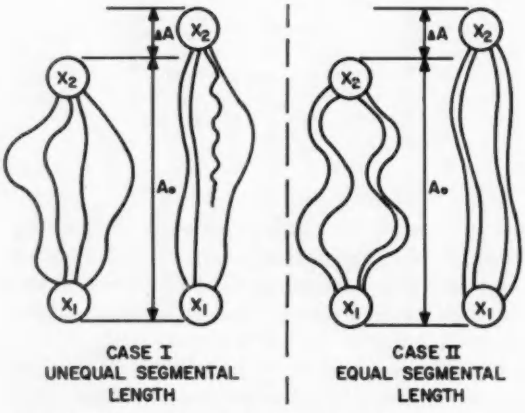

Fig. 1. Schematic presentation of molecular tautness.

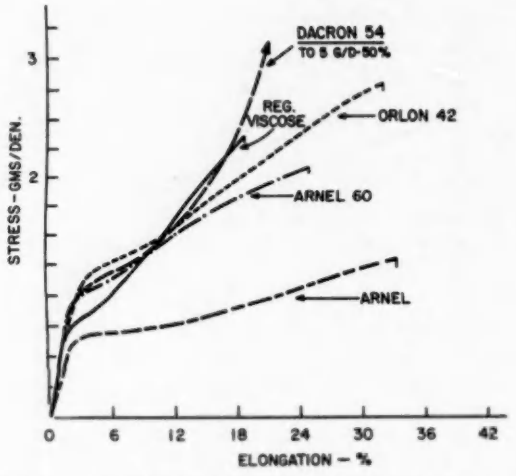

Fig. 2. Stress-strain behavior of various staple fibers at 23° C. and 65% RH.

Case I, unequal molecular segmental lengths lie between points of intermolecular attraction X_1 and X_2 which may be crystals or other points of secondary bonding. When this system is strained by $\Delta A/A_o$ the molecules become taut in a stepwise fashion; when the applied strain exceeds the excess length of the shortest molecule, that molecule is ruptured or is pulled out of the secondary bonding point X_1, whichever requires the smaller force. Accordingly, full cooperation among the molecules is never realized. In Case II, the molecules between X_1 and X_2 have equal lengths and therefore equivalent reactive forces when a strain $\Delta A/A_o$ is applied. Obviously this system is harder to rupture because of the greater degree of molecular cooperation. If a large number of such elements arranged in series-parallel are imagined, then a distribution of segmental lengths will exist, and the narrower that distribution, the more nearly will Case II be approached throughout the fiber.

To raise the strength of cellulose triacetate fiber, means were found to increase the molecular orienta-

TABLE I. Birefringence and Density of Arnel 60 in Comparison with Other Fibers

	Arnel 60	Arnel staple	Reg. viscose rayon	Fiber 40
Birefringence	0.034*	0.021*	0.028	0.042
Density, g./cm.³	1.299	1.300	—	—

* After saponification.

tion and improve the tautness distribution without a material change in the fiber crystallinity, giving the stress–strain behavior shown in Figure 2. Note that a tenacity in excess of 2 g./den. has been reached without a marked reduction in elongation over that found for Arnel triacetate and that the curve bears a striking similarity to those of Orlon 42 and Dacron 54 up to elongation of about 15%. This latter factor suggests that Arnel 60 may have hand and wrinkle performance characteristics roughly similar to acrylic and polyester fibers, when used in optimum constructions.

A measure of orientation and degree of crystallinity may be noted in Table I, which shows data on the birefringence of saponified fibers and on fiber density. Saponification is necessary to provide a measurable degree of birefringence and was carried out in the presence of sodium acetate at constant length to prevent swelling and disordering. The birefringences of regular viscose rayon and the high wet modulus rayon Fiber 40 are included for comparison. Note that the molecular orientation of Arnel 60, as estimated by birefringence, has been raised from the Arnel triacetate level to a level greater than that of regular viscose rayon but less than that of Fiber 40. The crystallinity, on the other hand, as estimated by fiber density, is very similar to that of Arnel triacetate.

The tautness distribution cannot be measured directly, but may be inferred from the stress–strain behavior. If the major increase in tenacity and modulus (nearly twofold) of Arnel 60 were due solely to the improved orientation, a considerable reduction in fiber elongation would be experienced. However, as was noted earlier, the elongation is rather similar to that of regular Arnel. Accordingly, we may assume that the cellulose triacetate molecules have been arranged in such a way that the free chain segments between points of intermolecular attraction are more nearly equal in length than in regular Arnel

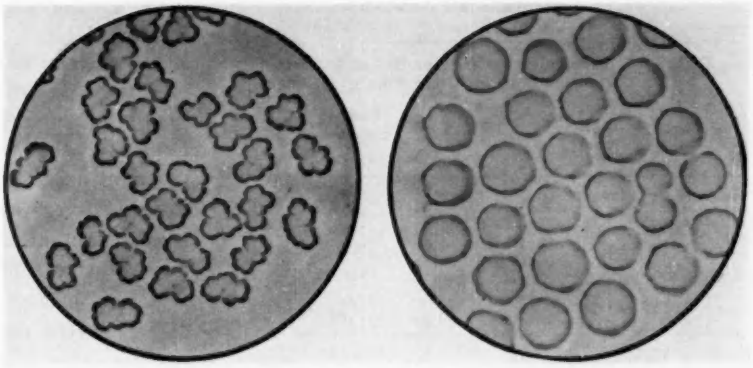

Fig. 3. Comparison of cross-sectional shape of Arnel staple, 2.5 den. (left) and Arnel 60, 3.0 den. (right).

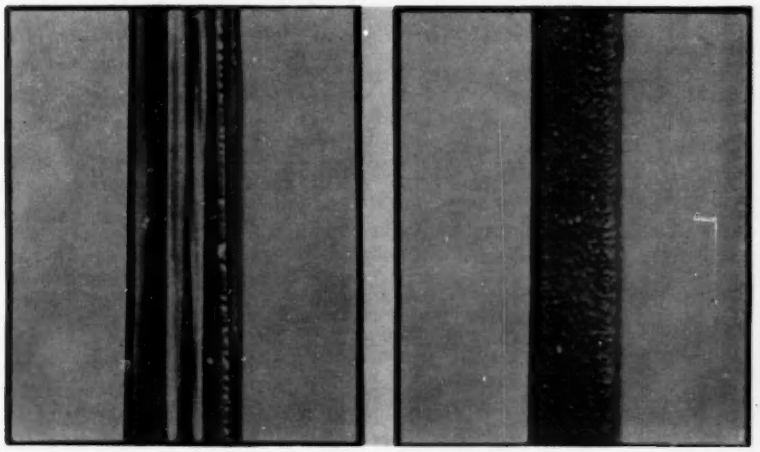

Fig. 4. Comparison of surface morphology of Arnel staple, 2.5 den. (left) and Arnel 60, 3.0 den. (right). Fibers shadowed with chromium.

but, on the average, have nearly the same amount of disorder as is found in regular Arnel.

Let us now examine the properties of the fiber having this fine structure.

Fiber Morphology

The typically round cross-sectional shape of Arnel 60, as compared to Arnel, is shown in Figure 3; longitudinal views of the same fibers are shown in Figure 4. Here the fibers have been shadowed with chromium to enhance surface detail and the rough textured surface of the Arnel 60 fiber is plainly visible. This surface has two distinct advantages in staple applications. It provides a semidull luster without the use of pigment and produces sufficient interfiber cohesion that satisfactory carding, drawing, and spinning may be carried out with only the low natural crimp present in the fiber.

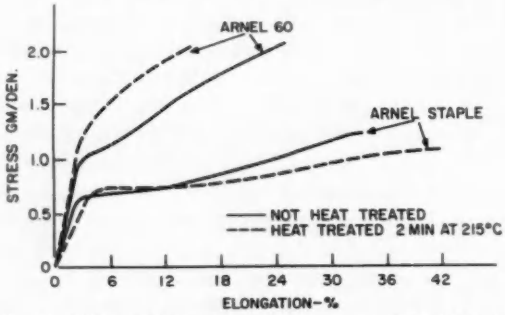

Fig. 5. Effect of heat treatment on stress–strain behavior of Arnel staple and Arnel 60.

TABLE II. Typical Tensile Properties of Arnel 60 in Comparison with Other Fibers

	Arnel 60	Arnel staple	Reg. viscose rayon	Fiber 40
Tenacity, g./den.				
23° C.–65% RH	2.1	1.2	2.7	3.0
23° C.-wet	1.5	0.8	1.4	2.0
Elongation, %				
23° C.–65% RH	25.0	34.0	21.0	9.0
23° C.-wet	36.0	45.0	24.0	10.0
Approx. yield stress, g./den.				
23° C.–65% RH	1.0	0.7	0.8	1.3
23° C.-wet	0.5	0.3	*	*
Modulus, g./den.				
23° C.–65% RH	49.0	28.0	44.0	83.0
23° C.-wet	28.0	13.0	3.0	6.0

* Too low to measure.

Tensile Properties

Typical tensile properties for Arnel 60 in comparison with other fibers are shown in Table II. While the dry properties are not equivalent to regular viscose rayon, the wet properties show considerable superiority, particularly in yield stress and modulus. The effects of moisture will be discussed in greater detail a little later.

The increased fiber tenacity of Arnel 60 is translated into improved spun yarn strength, as shown in Table III.

The effect of heat treatment on fiber stress–strain behavior is shown in Figure 5. Note that the behavior of Arnel 60 is quite unlike that of Arnel, the former becoming somewhat stiffer, particularly above the yield point, while the latter softens, decreasing in modulus and increasing in elongation. This difference in behavior is apparently due to the original microstructural differences in the two fibers. The Arnel 60, having greater orientation and considerably improved tautness distribution, is in a better position to crystallize rapidly before molecular relaxation occurs to a significant degree, whereas in Arnel the rate of relaxation appears to predominate. Some confirmation of this is obtained by examination of the x-ray diffraction patterns shown in Figure 6. The crystallites in the Arnel 60 are seen to

TABLE III. Typical Spun Yarn Properties for Arnel and Arnel 60

	Arnel	Arnel 60	Arnel 60
Denier-Staple length	2.5–2 in.	3.0–2 in.	1.5–1½ in.
Yarn count-Twist	18/1–14Z	18/1–14Z	30/1–21Z
Skein break, lb.	53.8	87.2	53.2
Skein break factor	965	1590	1610
Gram break	200	328	200
Gram break factor	3590	5990	6060
Tenacity, g./den.	0.68	1.13	1.14
Elongation, %	11.3	12.6	11.1
Fiber-to-yarn translation efficiency, %	56	55	54

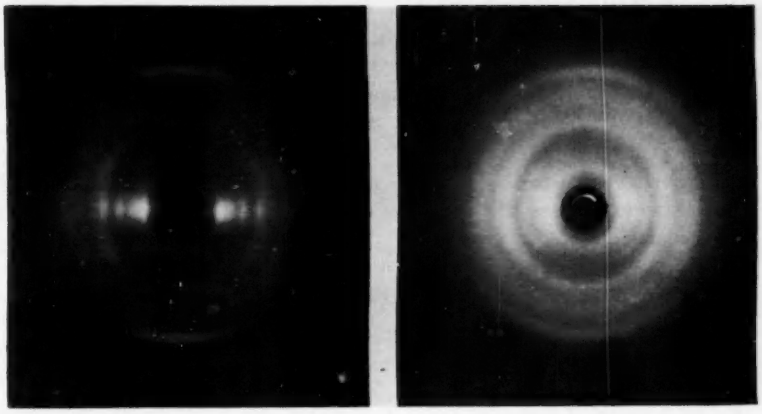

Fig. 6. X-ray diffraction patterns of Arnel 60 (left) and Arnel staple (right); fibers heat treated 2 min. at 215° C.

TABLE IV. Fiber Loop Properties

	Arnel 60	Arnel staple	Reg. viscose rayon
Straight tenacity, g./den.	2.1	1.2	2.7
Loop tenacity, g./den., as rec'd	1.0	0.7	0.8
After heat treatment*	0.6	0.5	—

* Heat treated 2 min. at 215° C.

TABLE V. Effect of Strain Rate on Tensile Properties

	Arnel 60	Arnel
Strain rate 60%/min.		
Tenacity, g./den.	2.1	1.2
Elong., %	25.0	29.0
Strain rate 500,000%/min.		
Tenacity, g./den.	2.3	1.4
Elong., %	11.0	8.0

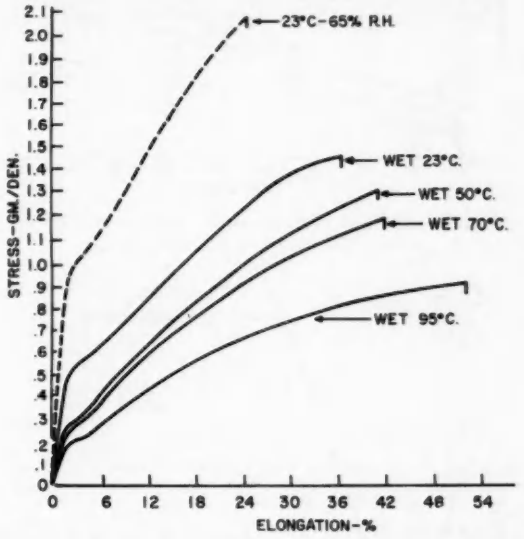

Fig. 7. Effect of moisture at various temperatures on stress–strain behavior of Arnel 60.

be better oriented and perfected than those in Arnel staple.

Some estimate of the lateral strength and ductility of a fiber may be obtained by examination of loop properties and the effect of strain rate on tensile properties. In Table IV, the loop properties of Arnel 60 are compared with those of Arnel and viscose rayon. The loop loss of Arnel 60 is seen to be intermediate between that of viscose and Arnel, with the absolute loop strength being higher than either. On heat treatment, the loop strength is further reduced but is still slightly greater than that of Arnel. In Table V, the effect of strain rate on tensile properties is shown. The data at 60%/min. were determined on an Instron tester while those at 500,000%/min. were obtained from a special tensile impact tester operating at 7.5 ft./sec. This high strain rate is thought to approximate the maximum rates to which fibers are subjected in textile processing. It will be noted that the effect of rate is similar in both Arnel 60 and Arnel, a reduction in elongation and a slight rise in tenacity being evident. The Arnel 60 is seen to be relatively ductile at the high strain rate, displaying 11% elongation, in spite of the higher orientation of this material.

Effect of Moisture

The effect of moisture at various temperatures on the stress–strain behavior of Arnel 60 is shown in

Figure 7. Note that the 70° C. span of temperature produces a considerable effect, but that a substantial modulus and yield stress is present even at 95° C. in water. This should result in good resistance to distortion in dyeing. Figure 8 gives data for Arnel staple which show behavior similar to Arnel 60 but at a lower level of stress. Figure 9 shows data for viscose rayon. Here the major effect occurs on wetting out, with water temperature being of relatively minor significance. Of particular importance from the standpoint of end use performance is the major reduction in modulus and the wiping out of the high yield point.

In Figure 10 are shown the stress–strain characteristics of various fibers in water at room temperature. The complete curves are not shown since the lower strain regions are the most important in end use. Note that the Arnel 60 is now somewhat less comparable to Dacron 54 and Orlon 42 in yield point, although similar in initial modulus. The Arnel 60 requires a relatively high level of stress to produce deformations of the order of 2–3%. Accordingly, excellent wet or humid creasing and

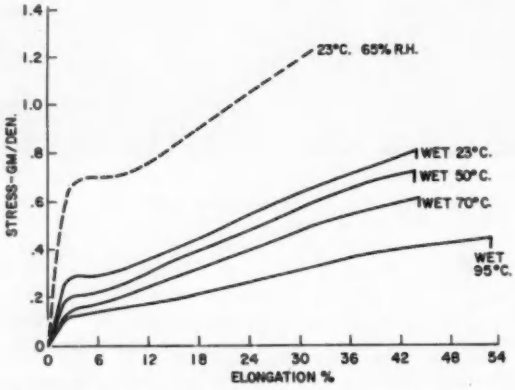

Fig. 8. Effect of moisture at various temperatures on stress–strain behavior of Arnel staple.

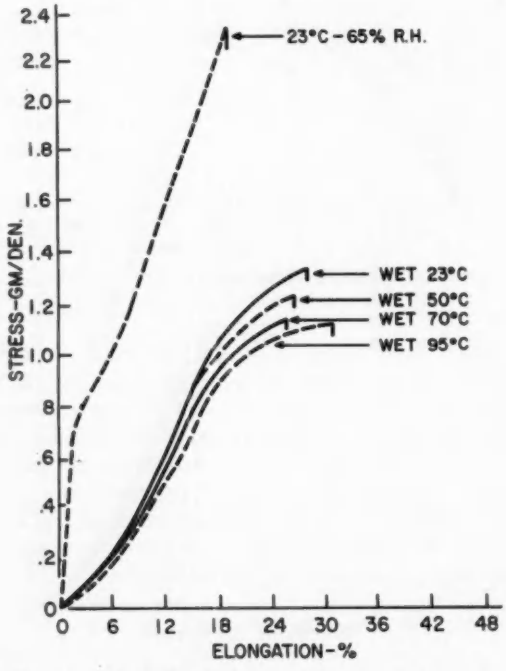

Fig. 9. Effect of moisture at various temperatures on stress–strain behavior of viscose staple.

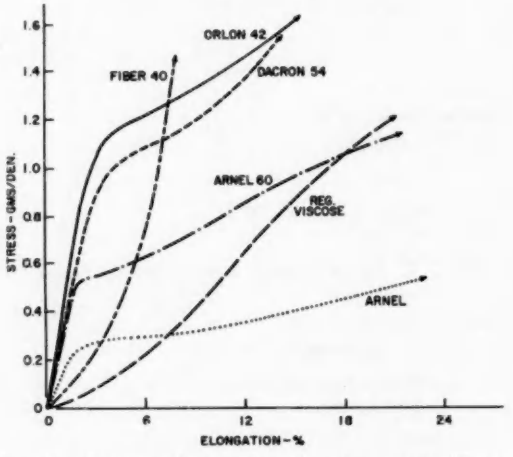

Fig. 10. Stress–strain behavior of various staple fibers in water at 23° C.

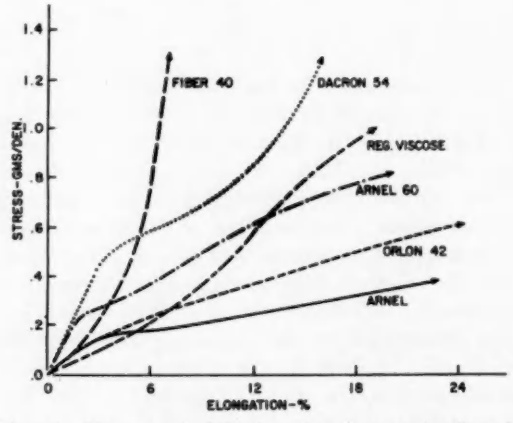

Fig. 11. Stress–strain behavior of various staple fibers in water at 70° C.

wrinkling resistance may be expected with this fiber without the use of resins.

Figure 11 shows similar data at 70° C. in water, which is about the maximum temperature to which garments might be subjected in laundering. The Arnel 60 is now distinctly superior to Orlon 42, as well as regular Arnel, in modulus and yield point. This suggests that Arnel 60 will show improved resistance to creasing and wrinkling during laundering.

The wet stress–strain data also indicate that Arnel 60 may be used to impart hot wet dimensional and form stability in blends with rayon or acrylics.

Miscellaneous Properties

The ironing and glazing behavior of Arnel 60 after heat treatment is similar to Arnel; that is, a safe ironing temperature of 230–240° C. and good resistance to glazing in both steam pressing and ironing.

The standard moisture regain of Arnel 60 is similar to that of Arnel, being 4.2% at 23° C. and 65% RH. After heat treatment this value is reduced to 3.3%. The water imbibition of Arnel 60, as determined by wetting out followed by centrifugation in an atmosphere at 100% RH, is 18.5%, falling to 16.8% after heat treatment. This is quite different from Arnel, which gives values of 14.2% and 9.8% before and after heat treatment.

The dimensional stability of Arnel 60 in hot water is excellent, the fiber shrinkage due to boiling in water for 30 min. being essentially zero. As was discussed earlier, the resistance of this fiber to stretching under hot wet conditions is also excellent.

Dyeing

It might be expected that perfecting the structure of a fiber sufficiently to approximately double its strength and modulus would have a substantial detrimental effect on the dyeing rate of the fiber. This is a well-known phenomenon with many other fibers such as polyamides, polyesters, acetate, and the acrylics. In this case, however, the dyeing rate of Arnel 60 is essentially equivalent to Arnel. This may be seen from Figure 12, where carefully controlled laboratory dyeings were made as a function of time. No significant differences were found between the Arnel and two lots of Arnel 60. Additional evidence of the equivalence of dyeing behavior is shown in Figure 13, which gives colorimetric data for a three-component brown shade after 1 hr. of

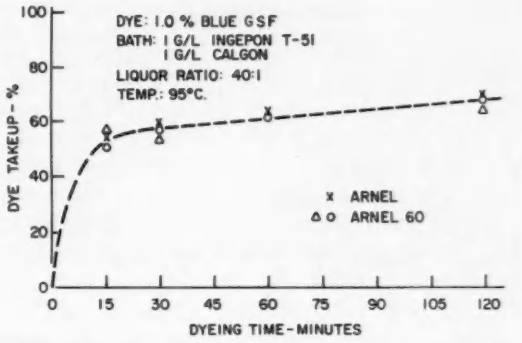

Fig. 12. Dye takeup vs. time for Arnel and Arnel 60.

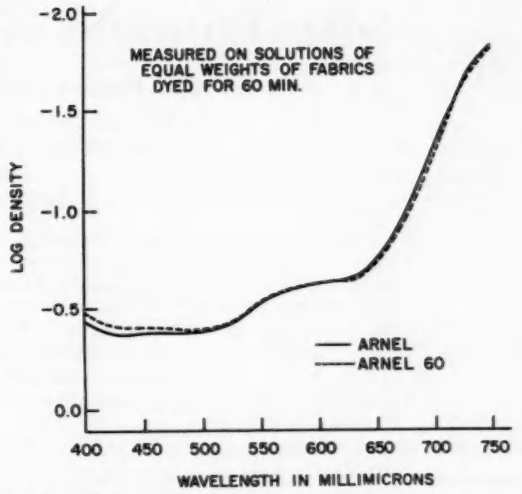

Fig. 13. Spectrophotometric measurement of the depth of shade achieved in winch dyeing of Arnel and Arnel 60.

dyeing in a standard winch operation. The curves for Arnel 60 and Arnel are almost identical.

Arnel 60 also responds to carriers in a manner similar to Arnel. The fastness behavior of dyed Arnel 60 is very similar to that of Arnel dyed with the same dyes.

The probable qualitative explanation for the similarity of dyeing behavior of Arnel 60 and Arnel lies in the fact that Arnel 60 is only moderately oriented and no more crystalline than Arnel, substantially deriving its improved properties from a narrower molecular tautness distribution. This change in tautness distribution and the increased orientation should have only a small effect on diffusion rate, which is apparently compensated for by the greater amount of surface of the Arnel 60 fiber due to its rough textured character.

Acknowledgment

The work connected with the development of this fiber has necessarily involved a great many people—more than can be acknowledged here. In this paper therefore, the author is merely acting as the spokesman for all those who have contributed to this project. The data and graphs utilized in this paper were largely developed by Mr. R. W. Singleton of the Summit Research Laboratories, Celanese Corporation of America.

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Some Principles of Nonwoven Fabrics[1]

Stanley Backer and Dewitt R. Petterson[2]

Textile Division, Mechanical Engineering Department, Massachusetts Institute of Technology

Abstract

The authors compare the mechanical behavior of woven and nonwoven fabrics. They outline the principal mechanisms by which woven cloths deform and recover in manufacture and in end usage. They attempt to formulate a parallel sequence of events in the distortion process for nonwovens and to show how these actions influence the ability of nonwovens to fit smoothly on three-dimensionally curved surfaces, to hang and drape freely, and to recover from bends and tensile extension.

Some results of a research program recently conducted at M.I.T. on nonwovens are presented. This study is related to the directional tensile behavior of nonwoven fabrics and demonstrates how knowledge of fiber properties and web structure can be used effectively to predict web behavior. Fiber behavior measured on the Instron provide the material constants necessary for insertion in derived analytical expressions for nonwoven fabric stiffness and contraction ratios. Predicted nonwoven behavior shows reasonable agreement with experimental measurements on the particular materials studied.

THE TERM nonwovens is applied to weblike assemblages of textile fibers wherein fiber-to-fiber bonding replaces twisting and interlacing as a means of developing strength and recoverable extensibility. The range of materials bracketed by the term nonwoven includes structures which are stiff, dense, two-dimensional, and paperlike as well as materials which are thick, highly extensible, and highly porous. Clearly the behavior of such assemblages will be determined by a complex interaction between fiber properties and bond characteristics. In some cases the behavior of the bond will dominate the character of the nonwoven; in other cases the fibers—their geometry and mechanical properties—will call the tune.

We shall not attempt to deal with the full range of materials which can be classified as nonwovens, nor with the behavior of both bond and fiber. Rather, we shall direct our attention towards that grouping of nonwovens which is designed to emulate thin apparel wovens, whether for reasons of physical superiority or of lower costs. The principles of which we speak are primarily the mechanical principles of deformation of nonwovens and our approach will be based to a major extent on the contribution of the fiber component rather than on the influence of the bond.

Woven fabrics designed for apparel usage mani-

[1] Presented at the 30th Annual Meeting of Textile Research Institute, New York City, March 25, 1960.

[2] Present address: Chicopee Manufacturing Co., Milltown, N. J.

fest characteristic resistances to the stresses of manufacturing and usage. For each type of force application they have a unique extensional response quite unlike the response of solid sheet materials to (1) uniform two-dimensional stresses, (2) uniform bending (into the third dimension), and (3) stress concentration, both in and out of the fabric plane. The reason for this uniqueness of response to the three named modes of force application lies with the particular mechanisms which dictate the nature of the deformation in an interlaced structure comprised of twisted fiber bundles. If we are interested in designing a nonwoven fabric to emulate a woven cloth for apparel uses, it will be worth while to contrast the behavior of the bonded sheet to that of the woven material when subjected to uniform planar stresses, to uniform bending, and to stress concentrations. Where major differences in the mechanisms of deformation occur between woven and nonwoven, it may be necessary to devise alternate routes in the design of the nonwoven to simulate the behavior of the woven material. On the other hand, it may be necessary to restrict the application of the nonwoven to particular uses of woven cloths, indeed to uses where the performances of the nonwoven may far excel that of the conventional woven structure.

The application of two-dimensional stresses to a woven fabric may include uniaxial tension, uniaxial compression, biaxial tension and/or compression, and planar shear as well as a combination of tension, compression, and shear. For simplicity we choose the case of uniaxial tension at a slight angle to warp or filling, and find the mechanisms of woven fabric deformation to be:

1. Thread shear
2. Crimp interchange
3. Yarn flattening
4. Yarn compaction
5. Fiber rotation
6. Fiber extension

while the mechanisms of nonwoven fabric deformation are those of:

1. Fiber rotation
2. Fiber straightening
3. Bond rotation
4. Bond extension
5. Fiber extension

It can be argued that with crimped or stretch yarn the mechanism of fiber straightening is important in woven fabric deformation, and there are in fact, many other mechanisms operative within both woven and nonwoven systems other than those cited above. But the list provided is useful in pointing out the presence of at least four (1–4 inclusive) woven fabric distortion mechanisms which do not exist in the nonwoven, mechanisms which account for major dimensional changes with little or no resistance, hence with little expenditure of elastic strain energy. Further, the important mechanism of thread shear or rotation of warp and filling relative to one another is characteristic only of the woven fabric. It is this mechanism which is so active in the fitting of a two-dimensional cloth to a three-dimensional surface and in providing local reductions in area necessary for such fitting.

Bending of a woven fabric calls on the following mechanisms of deformation in varying degrees, depending on yarn and fabric structure:

1. Local crimp interchange
2. Yarn buckling at the bend
3. Yarn flattening
4. Yarn compaction
5. Fiber slippage
6. Fiber rotation
7. Fiber extension
8. Fiber bending

while in nonwovens the mechanisms of deformation at a bend are seen as:

1. Fiber rotation
2. Fiber straightening in the fabric plane
3. Bond rotation
4. Fiber buckling at the bend
5. Fiber bending out of the fabric plane
6. Bond bending

Here again we see at least five distortion mechanisms present in the woven fabric behavior, from local crimp interchange to fiber slippage, which require little or no elastic strain energy and afford a low order of resistance to the bending forces.

Finally, in viewing the reaction of woven and nonwoven fabrics to stress concentration, we observe the reaction of a woven fabric to stress concentration along a single yarn as involving:

1. Extension of the longitudinal yarn in contact with the outside stress

2. Local displacement and rotation of adjacent cross yarns
3. Stress transfer from rotated cross yarns to adjacent longitudinal yarns

The reaction of woven fabric to stress concentration across a single yarn differs slightly and includes:

1. Bending and extension of the lateral yarn in contact with the outside stress
2. Slippage of the lateral yarn and jamming against other lateral yarns
3. Transfer of stress to other longitudinal yarns at the points of jamming

On the other hand, the reaction of a nonwoven fabric to stress concentration such as is met in a localized pull or puncture involves:

1. Rotation of contact fiber
2. Bending of contact fiber
3. Extension of contact fiber
4. Collection of other fibers in path of movement of the stress point

Here the principal difference between woven and nonwoven lies in the fact that the initial stress application to the structural unit (yarn in a woven, fiber in a nonwoven) is followed by a high degree of slippage and dislocation in the woven structure. This movement forces the involvement of neighboring yarn elements in the stress pattern well before the initial yarn has reached its limit of stress capacity. In the nonwoven, the collective involvement of adjacent fibers depends entirely on the extensibility of fiber and bond and is therefore quite limited. In short, the woven structure is in a better position than the nonwoven to withstand punctures, tears, stitch gatherings, and stress transfers in a fabricated garment and other forms of stress concentration met in service. Of course this refers to stress concentration at a respectable distance from a free (unstitched) edge, which might otherwise involve yarn slippage and thread unraveling in a woven structure.

A desirable woven fabric used for apparel applications (as the outer cloth) must have adequate dimensional stability in manufacture of the garment and in its usage and servicing (laundering or dry cleaning). It must have low bending rigidity—ability to bend and drape under its own weight—but it must not be limp. It must have high area deformability to accomodate curvatures in three dimensions. It must have good recovery from extensions and bends—but not rubberlike recovery. It must be durable and resistant to tears and stress concentrations. Of course the desired levels of each property cited above will vary with the garment application, with the position of the cloth in the garment structure, and with the classification of the cloth and what the consumer expects from it (say a tweed versus a worsted material). There are, no doubt, innumerable other properties of woven fabrics which have been the subject of separate researches and which are of importance to the merchandising potential of apparel textiles. But we have limited our consideration to the properties cited above, for they serve to illustrate the essential differences in wovens and nonwovens as we know them today. These differences can be broadly attributed to the variance in mechanism of deformation of the two textile structures.

In general it can be said that the woven structure can accomodate normal tensile and bending strains in the direction of its yarns with little fiber strain. Thus it meets the consumer's concept of desirable softness and drape and at the same time satisfies the need for dimensional stability. The nonwoven calls for fiber straightening followed by fiber extension at a very early stage of fabric extension; the resultant work required to stretch the fiber disturbs the wearer's feeling of softness or drape. On the other hand, if the nonwoven is made of a highly elastic (good recovery) fiber and the bonding is likewise highly elastic, the added resistance to slight extension of the nonwoven fabric will be accompanied by improved recovery in tension, compression, and in bending—thus lending the makings of a good lining or stiffening fabric for many garment applications.

The high degree of fiber and yarn freedom in the woven fabric likewise pays off in deformability of the fabric to the three-dimensional shape of the garment. Taking a sheet material from two dimensions into the third dimension is accomplished by two principal actions: bending and area modification. The bending action is obvious. The area modification can be accomplished by three routes: by increase in area through stretching, by decrease of area through in-plane compression, or by reduction of area through local shearing. The structure of the woven fabric lends itself easily to in-plane compression (as at the shoulder sleeve seam) and to thread shear (visible when one stretches a

copper window screening over a spherical surface). The typical thin semi-isotropic nonwoven cannot easily accomodate in-plane compression without buckling or wrinkling, and it lacks the easy shear avenue present in an orthogonal interlaced yarn system. The shear rigidity of the nonwoven is of greater utility in the lining or stiffener application mentioned above than in the usual outer cloth of a garment.

Finally, the ability of the woven structure to shift points of stress application so as to "rope-up" yarn bundles at a tear or snag contributes immeasurably to its durability as an outer fabric in garments. The corresponding inability of nonwovens to spread the stress concentration leads to their early breakdown in outer wear or early irreversible dimensional changes.

Can anything be done to overcome the weaknesses which have emerged as characteristic of nonwovens as contrasted to woven structures used for apparel materials? We believe the answer is affirmative, for many of the desirable features of woven cloth deformation can be simulated by manipulating the structure of the nonwoven according to studied designs. The bunching of fibers in a structural nonwoven pattern has, in a way, simulated the roping effect of the woven cloth. The creping of papers intended for structural reinforcement of plastic articles has shown how flexibility and shape conformability can be improved through provision of local area increases with slight tension. The introduction of highly elastic and tough fibers and equally elastic and strong bonds has demonstrated that nonwovens can be made durable and resilient. On the other hand, we feel that full quantitative understanding of the mechanisms of deformation of woven and nonwoven systems is essential to permit more effective design of useful and physically competetive nonwoven materials. Such an understanding will have additional practical utility in defining the expected limits of nonwoven structural behavior and in avoiding costly empirical researches along lines devoid of physical potential.

An example of a combined analytical and experimental approach to the understanding of the physical behavior of nonwoven structures is the recent research conducted at the Textile Division Laboratories at M.I.T. under a Grant-in-Aid from the Union Carbide Chemicals Company. A full account of this study will be reported in a series of separate papers, but it is sufficient for now to outline the objectives of the research, the assumptions made in the analysis, the analytical results, and the agreement between theory and experiment.

The objectives of the research were:

1. To test the elastic theory of orthotropic materials in prediction of directional material constants of a nonwoven. In short, if information is given about the modulus of elasticity, the shear modulus, and the contraction (Poisson) ratio in two principal directions of a material, can we predict its behavior when subjected to stresses in directions other than its "grain" or machine direction—or transverse direction?

2. To develop a fiber web theory for an ideal material or, given the stress–strain properties of the fiber and its distribution in the web, can we predict all the directional mechanical constants of the nonwoven? This latter theory would be a far more powerful tool than the conventional orthotropic theory, since it would allow complete design of a new structure and prediction of its properties without initial empirical studies.

3. To modify the fiber web theory for treatment of a real material. Here we must take into account the variability in fiber properties, the nonuniformities in density of the fiber spread, and the variations in orientation from place to place in the web.

The theory of orthotropic materials is well developed in the classical literature of elasticity [2] and is readily applied to single sheets and multiple structures of plywood. The theory assumes that a stress–strain relationship is given for the two principal directions of the material. It further assumes the limitations of small elastic strains. If the mutually perpendicular principal material directions are designated as 1 and 2 and the directions at any angle to the 1 and 2 directions are designated simply as x and y, the problem can be simply stated as follows:

Given the elastic moduli E_1, E_2, the shear modulus, G_{12} and the contraction ratio μ_{12}, determine E_x, E_y, G_{xy}, and μ_{xy}, or determine the normal and shear strains ϵ_x, ϵ_y and γ_{xy} which result from the normal and shear stresses σ_x, σ_y, and τ_{xy}.

The solution then follows in three steps: (A) transposition of the given stress σ_x, σ_y, and τ_{xy} using Mohr's circle for equilibrium of stresses, to the principal directions, giving σ_1, σ_2, and τ_{12};

(B) use of given stress–strain relationships to determine strains ϵ_1, ϵ_2, and γ_{12}; (C) use of Mohr's strain circle to transpose strains to the original direction, giving ϵ_x, ϵ_y, and γ_{xy}. The combination of all three steps into a single stress–strain relationship takes the following form:

$$\epsilon_x = b_{11}\sigma_x + b_{12}\sigma_y + b_{13}\tau_{xy} \quad (1)$$

$$\epsilon_y = b_{21}\sigma_x + b_{22}\sigma_y + b_{23}\tau_{xy} \quad (2)$$

$$\gamma_{xy} = b_{31}\sigma_x + b_{32}\sigma_y + b_{33}\tau_{xy} \quad (3)$$

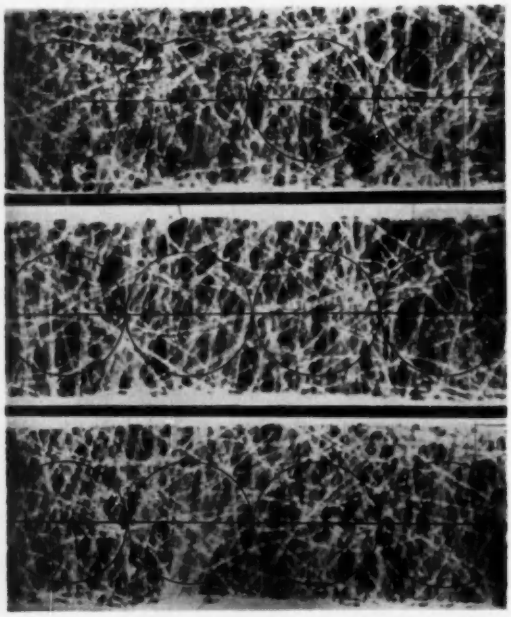

Fig. 1. Specimen of nonwoven used in evaluation of orthotropic theory and fiber web theory.

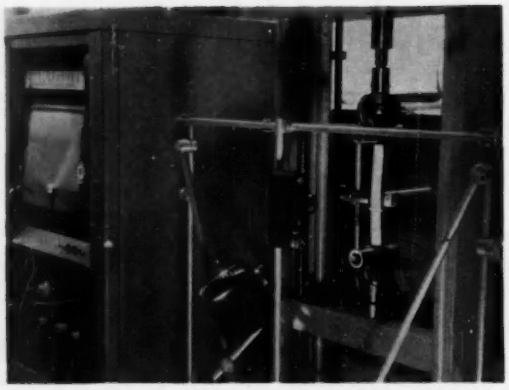

Fig. 2. Experimental setup for measuring mechanical properties of nonwoven specimens.

where the coefficients b are functions of E_1, E_2, G_{12}, and μ_{12}. If a uniaxial stress σ_x is applied in the x direction, the apparent modulus E_x may be determined from Equation 1 as σ_x/ϵ_x. If σ_y alone is applied, E_y follows from Equation 2. μ_{xy} (contraction in the x direction following uniaxial stress in the y direction) is determined from Equations 1 and 2 as ϵ_x/ϵ_y when σ_y is given and $\sigma_x = \tau_{xy} = 0$. G_{xy} is determined from Equation 3.

To check out the predicted values of modulus of elasticity and contraction ratio for the nonwoven pictured in Figure 1, use has been made of a table model Instron. A test sample 8 × 1 in. has been cut at various angles to the machine direction of the nonwoven and a square grid was imprinted on the center section of the material specimen. The distortion of this grid was photographed during the test and served as a measure of longitudinal extension and transverse contraction during the tests; see Figure 2.

Test results for the specific modulus E_y of Fabric A (given in grams/denier) are shown in Figure 3

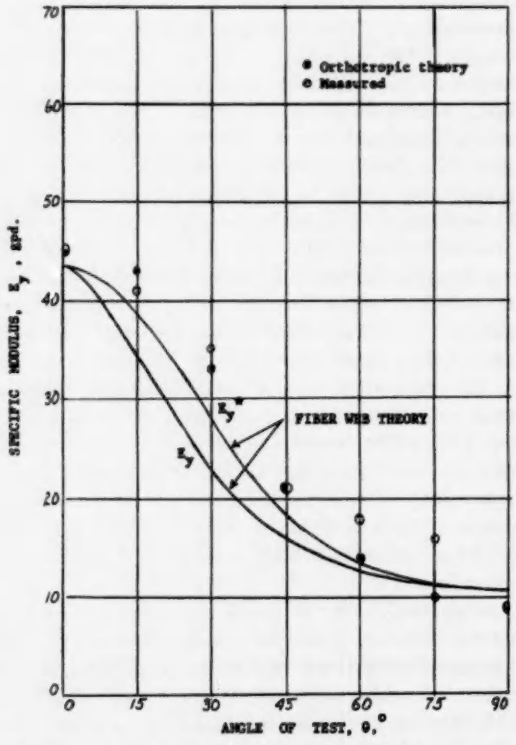

Fig. 3. Initial specific modulii, Fabric A. Measured, orthotropic, and fiber web theory.

as open circles. The predictions of orthotropic theory are shown as solid circles and are seen to be in good agreement with the measured data. The contraction (Poisson) ratios μ_{xy} measured for Fabric A at various angles are shown as open circles in Figure 4, while the predictions of μ_{xy} from orthotropic theory are shown as closed circles. The agreement between orthotropic theory and measurement is fair.

It should be emphasized that the applicability of the orthotropic theory must be further established for nonwoven materials which differ significantly from the viscose rayon nonwoven bonded with viscose, shown in Figure 1. But even with an established broad validity in nonwovens, the orthotropic theory has definite limitations to its usefulness. It does not allow for complete design of the nonwoven starting with the fiber elements and progressing through the structural geometry of the materials. It does not permit of prediction of both elastic and plastic fiber behavior in the web.

In furtherance of this research, a fiber web theory

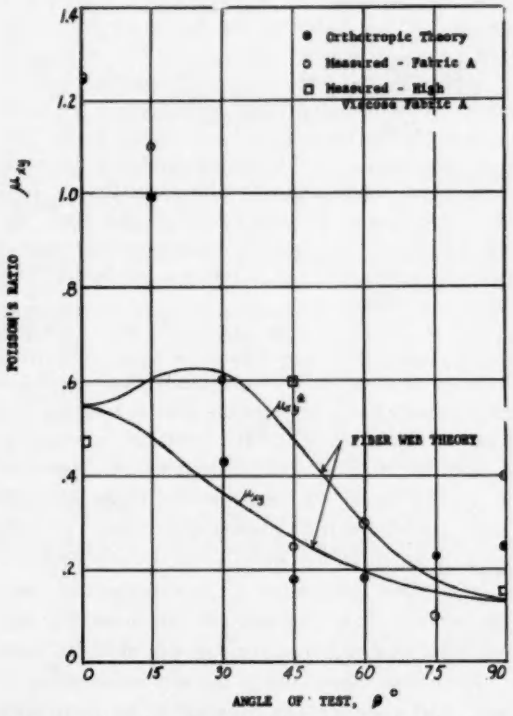

Fig. 4. Poisson's ratios, Fabric A. Measured, orthotropic, and fiber web theory.

was developed to accomodate the broad mechanical design requirements of nonwovens. Patterned after theories developed for yarns by Platt [3] and for paper by Cox [1], the fiber web theory assumes the stress–strain properties of the fiber to be given. It likewise assumes a distribution of fibers in terms of orientation relative to the machine direction of the nonwoven. The bonding strength is considered to exceed the rupture strength of the fibers. The fibers are assumed to be straight. Fiber properties and fiber orientations are taken to be uniform from point to point in the fabric. The fabric is considered to be subjected to a longitudinal strain and the appropriate relationship between fabric strain ϵ_y and the strain ϵ_β of a fiber lying at an angle β to the direction y is shown to be

$$\epsilon_\beta = \epsilon_y(\cos^2\beta - \mu_{xy}\sin^2\beta) \tag{4}$$

where μ_{xy} is the fabric contraction ratio for the x–y directions. The stress contribution of this given fiber to the fabric y-direction is then determined from knowledge of its stress–strain behavior. The number of fibers lying at the angle β is determined from the known orientation distribution of the fiber population. The stress contribution of all fibers to the fabric y-direction is shown to be

$$\sigma_y = E_f\epsilon_y\int_{-\pi/2}^{+\pi/2}[\cos^2\beta - \mu_{xy}\sin^2\beta]\cos^2\beta\phi(\beta)d\beta \tag{5}$$

where E_f is the fiber modulus, σ_y is the nonwoven fabric stress in the y-direction, and $\phi(\beta)$ is the distribution function of the fibers relative to the angle β between the fiber and the y-direction.

The stress build-up in the x-direction is shown to be

$$\sigma_x = E_f\epsilon_y\int_{-\pi/2}^{+\pi/2}[\sin^2\beta\cos^2\beta - \mu_{xy}\sin^4\beta]\phi\beta d\beta \tag{6}$$

and since we consider a uniaxial loading in the y-direction,

$$\sigma_x = 0 \tag{7}$$

from which it follows that

$$\mu_{xy} = \frac{\int_{-\pi/2}^{+\pi/2}\sin^2\beta\cos^2\beta\phi(\beta)d\beta}{\int_{-\pi/2}^{+\pi/2}\sin^4\beta\phi(\beta)d\beta} \tag{8}$$

Thus the contraction ratio is shown to be dependent on fiber geometry alone—assuming no fiber buck-

ling. From Equations 5 and 8 an expression is derived for E_y

$$\frac{E_y}{E_f} = \int_{-\pi/2}^{\pi/2} \left[\cos^4 \beta - \cos^2 \beta \sin^2 \beta \times \frac{\int_{-\pi/2}^{\pi/2} \sin^2 \beta \cos^2 \beta \phi(\beta) d\beta}{\int_{-\pi/2}^{\pi/2} \sin^4 \beta \phi(\beta) d\beta} \right] \phi(\beta) d\beta \quad (9)$$

Equations 8 and 9 give us values for stiffness and the contraction ratio of the fiber web when tested uniaxially in the y-direction. An implicit assumption in the derivation is that the angle $\beta = 0$ designates the y-direction of pull and also represents a symmetric axis of the fiber orientation distribution. In other words, it has been assumed that a tensile strain ϵ_y can be applied to the web, resulting in a uniaxial stress σ_y only; no γ_{xy} or τ_{xy} will occur. However, if the axis of pull and the axis of fiber orientation symmetry do not coincide, an extension ϵ_y exerted on the web by jaws of the Instron tester will be accompanied by either a shear stress τ_{xy} (if the jaws are not allowed to rotate) or a shear strain γ_{xy} if the jaws are allowed to rotate. The Instron tests actually provide a mixture of these conditions. It is essential therefore to consider both conditions of test in continuing the analysis of stiffness, contraction ratio, and shear modulus and in treating all directions of pull relative to the symmetry axes of the nonwoven. This analysis has been completed; the results are presented in Figures 3 and 4. The E_y^* of Figure 3 corresponds to the stiffness value predicted for the case of zero jaw rotation in the Instron; the theoretical E_y value represents the true uniaxial modulus of the web in the y-direction where freedom of jaw rotation is permitted; that is, no shear stress τ_{xy} is allowed to develop. It is seen that the E_y^* analysis based on the condition of no jaw rotation is closer to the measured values of modulus at the various angles of test (indicated by the open circles).

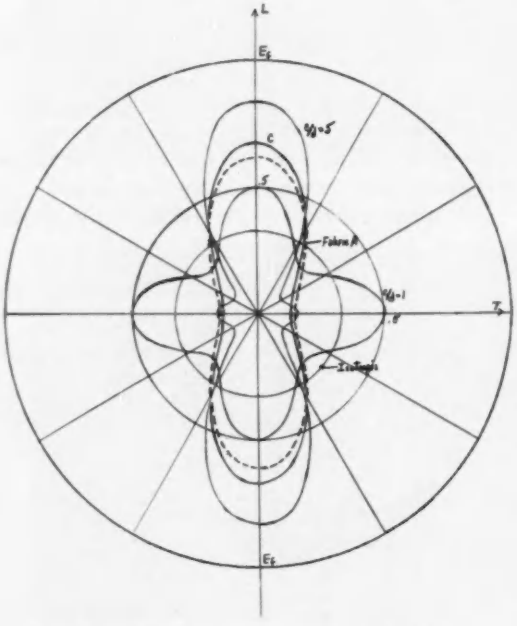

Fig. 5. Specific modulii of assumed distributions vs. angle of test.

In Figure 4 we note a considerable disagreement between the measured values for the Poisson's ratio (open circles—Fabric A) and the theoretical curves for both μ_{xy} and μ_{xy}^*. Since the analysis assumed no fiber buckling, it was suspected that there was insufficient binder (1–2% regenerated viscose solution based on the weight of the viscose fiber—regular tenacity, $1\frac{1}{2}$ den., $\frac{1}{4}$–$\frac{3}{8}$ in. in length). Accordingly, the web was reimpregnated and the binder content significantly increased in an effort to increase the number of bond points in the web and thus reduce the buckling tendency of fibers lying at a large angle to the direction of pull. Measurements of Poisson's ratio of the High Viscose Fabric A are shown in Figure 4 as open squares and are in much closer agreement with the theoretical μ_{xy}^* values.

Similar success was recorded in predicting mechanical properties of a second nonwoven material, leading to the conclusion that the Fiber Web Theory has a strong potential in treating this type of short straight-fiber, wet-laid nonwoven. It remains to be seen as to how the analysis can be applied as is, or extended to cases of more conventional textile nonwovens. But at this stage the analysis has merit in providing a picture of nonwoven properties as a function of fiber orientation. Take, for example, the case of a web comprised of two perpendicular sets of fibers, each of which has essentially a parallel orientation in itself, and consider the bundles to be comprised of c and d fibers. The c fibers are intimately

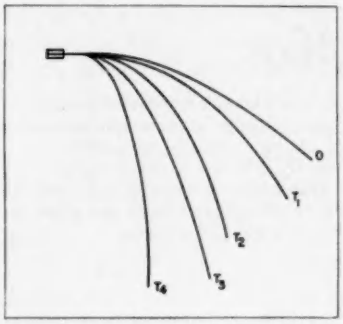

Fig. 6. Effect of planar compression on bending stiffness of a nonwoven (0 is original; T_1–T_4 are successively higher levels of planar compression).

mixed with the d fibers in the web plane. By varying c relative to d we can anticipate fabric behavior such as is pictured in the polar diagram of Figure 5. Here one observes a comparison of directional moduli among postulated behaviors for various c/d ratios and isotropic behavior and measured behavior of Fabric A.

The properties calculated for $c/d = 1$ come closest to matching the behavior of a woven fabric with stability in warp and filling directions and low dimensional stability on the bias, corresponding to high shear deformability. This does not imply that a nonwoven constructed with $c/d = 1$ will have the softness and drape of a woven fabric, but, as stated before, the fabric can be manipulated mechanically in an extension–planar compression cycle to improve its hand. Cyclic treatment of the type indicated is shown in Figure 6, which portrays the actual profile of a simple cantilever bending test of an untreated nonwoven and of the same nonwoven after mechanical treatment cycles T_1, T_2, T_3, and T_4. The potential improvement is manifest.

Summary

In this paper we have compared the mechanical behavior of woven and nonwoven fabrics. We outline the principal mechanisms by which woven cloths deform and recover in manufacture and in use. An attempt is made to formulate a parallel sequence of events in the distortion process for nonwovens and to show how these actions influence the ability of nonwovens to fit smoothly on three-dimensional curved surfaces, to hang and drape freely, to hold their shape, and to recover from tensile and bending deformation. The need for a wider study of the macro and micro mechanics of nonwoven fabric behavior is stressed.

The results of a research program recently conducted at M.I.T. on nonwovens are presented as an illustration of successful mechanical analysis of the properties of certain nonwoven structures. This study is related to the directional tensile behavior of nonwoven fabrics and demonstrates how knowledge of fiber properties and web structure can be used effectively to predict web behavior. Both elastic and plastic tensile fiber behavior measured in the Instron can provide the material constants necessary for insertion in derived analytical expressions for nonwoven fabric stiffness, contraction ratio, and even for yield stress and rupture stress. The role of fiber orientation is treated in the analysis. A graphical comparison is made of the mechanical behavior of several nonwoven structures, and their approach to woven fabric behavior is cited. An example of a technique of improving the hand of nonwovens is given.

Acknowledgments

The support of the Research Department, Union Carbide Chemicals Company through a Grant-in-Aid to the Textile Division, M.I.T. is gratefully acknowledged. The specific analysis reported forms part of Dr. Petterson's Sc.D. thesis presented in the Department of Mechanical Engineering, M.I.T., August 1958.

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Letters to the Editor

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Action of Dimethyl Sulfoxide on Wool

Western Regional Research Laboratory [1]
Albany 10, California
March 17, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Dimethyl sulfoxide, by virtue of its ability to penetrate wool, is a promising medium for wool treatments. A limitation for such treatments is that dimethyl sulfoxide, under certain conditions, causes wool fibers to supercontract. Under extreme conditions the supercontraction is accompanied by excessive mechanical degradation and decreased resistance to chemicals. The supercontraction, under controlled conditions, is a possible chemical means for processing felts. This note deals with information needed on the conditions and features of supercontraction by dimethyl sulfoxide.

It is well known that other reagents also cause wool fibers to supercontract to less than their original length [1, 3, 4]. These include certain inorganic salts (lithium bromide, for example) in concentrated aqueous solution; reagents that split disulfide bonds (for instance, hot aqueous sodium bisulfite), and organic compounds (such as phenol) that break hydrogen bonds. These reagents can cause supercontraction up to about 50%.

Dimethyl sulfoxide is attracting commercial interest as an inexpensive, high boiling (189° C.), nontoxic liquid of tremendous solvent power, nearly colorless and odorless, and stable except for slight decomposition at its boiling point [5]. The high dielectric constant and hydrogen bond forming tendency [2] of dimethyl sulfoxide probably contribute to its ability to supercontract wool.

In the following experiments, wool from Columbia and Lincoln sheep were used for single fiber tests. The fabric was undyed flannel exhaustively extracted with ether followed by ethanol. Dimethyl sulfoxide was a commercial grade, reported to be 99.9% pure.

Individual fibers contract in length about 28% when heated with dimethyl sulfoxide at 105° C. for 1 hr. Wool fibers under slight tension were conditioned (21° C., 65% RH) and cut to 3-in. lengths. The loose fibers were then heated in dimethyl sulfoxide, rinsed a few times with warm acetone, reconditioned, and remeasured. In 5 min. at 105° C., the reduction in length was 4.3%; in 50 min. it was 27.6% (average of 28.3, 26.7, and 27.7). At 85° C., only 7% length reduction occurred in 30 min.; hence,

TABLE I. Comparative Analyses of Untreated and Dimethyl Sulfoxide-Treated Wool Flannel

	Analytical values, %	
	Untreated wool control	Dimethyl sulfoxide-treated wool, 1 hr., 105° C.
Total nitrogen*	16.7	16.7
Amino nitrogen*†	0.34	0.35
Total sulfur*	3.39	3.44
Acid solubility‡	8	16
Alkali solubility**	10	18

* Calculated on a dry wool basis.
† Van Slyke method.
‡ In 4 *M* HCl, 1 hr., 65° C.
** In 0.1 *M* NaOH, 1 hr., 65° C.

[1] A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

temperatures of 100° C. or higher are indicated for practical applications. For comparison, fibers heated in dimethylformamide at 105° C. contracted in length 1% in 5 min. and also only 1% in 50 min.

Weighed swatches of wool flannel were placed in trays with sufficient dimethyl sulfoxide present to cover the fabric. A thin glass plate was placed on the fabric to prevent it from curling out of the liquid during treatment. The tray with sample was heated in an oven at 105° C. for 1 hr. The treated fabric was washed with warm acetone and then extracted with ethanol overnight in a Soxhlet apparatus. No significant weight changes occurred. The results of analyses of treated and untreated samples, given in Table I, show that the 1-hr. treatment has no appreciable effect on the total nitrogen, amino nitrogen, or total sulfur content. These data, together with the observed constancy in weight, appear to exclude any significant chemical modification of the wool. Even minor addition of dimethyl sulfoxide would be detectable, since the sulfoxide contains no nitrogen and 41% sulfur. It appears that hot dimethyl sulfoxide promotes the rearrangement of wool's structure in such a manner as to shorten the fiber and lower the resistance to attack by acid and alkali.

To investigate the physical properties of dimethyl sulfoxide-treated fabrics, samples of flannel were heated with this reagent at 105° C. for 0.5, 1, or 2 hr. by the previously described procedure. For reference, a sample of flannel was heated dry at the same temperature for 2 hr. and then extracted. The fabric properties are summarized in Table II. Fabric shrinkage up to 36 area percent is produced by dimethyl sulfoxide treatment. This shrinkage, since it occurs in the absence of mechanical agitation, is the result of fiber supercontraction and thus differs from felting shrinkage, which results from fiber migration. The fabric shrinkage is accompanied by increased fabric density. The treatment applied to pressed felts gives denser felts without the mechanical compression usually required.

Table II also shows that the treatment of wool flannel causes a progressive decrease in wet and dry breaking strength and in dry tear strength; there are also changes in elongation at break. The fabric becomes less flexible, and it recovers from wrinkling somewhat less readily than untreated wool.

After a 2-hr., 105° treatment, followed by extraction of the dimethyl sulfoxide, the scales are intact and the cortex is not separated. The fibers are swelled roughly 10% in cross-sectional area. The treatment also causes a marked drop in birefringence of longitudinally-viewed fibers, suggesting that dimethyl sulfoxide penetrates oriented portions of the fiber and reduces the molecular orientation and crystallinity. This loss of orientation is supported by the x-ray diffraction patterns of treated fibers. The sharp arc at 5.15 Å, typical of the α pattern of normal wool, is replaced by a diffuse ring at 4.60 Å, indicating that the configuration of the polypeptide chain is β and that the chains are loosely packed in a random fashion. Similar rearrangements of wool structure have been noted in other cases of supercontraction [1].

In summary, the supercontraction of wool with hot dimethyl sulfoxide is believed to result from physical rearrangement of the polypeptide chain. Treatment for more than about ½ hr. at 105° C. seriously weakens the wool in mechanical strength and in resistance to acids and alkalis.

TABLE II. Properties of Wool Flannel Treated with Dimethyl Sulfoxide at 105° C.

	Control	Dimethyl sulfoxide-treated		
Treatment time, hr.	2.0	0.50	1.0	2.0
Treatment shrinkage, area %	0	19	28	36
Fabric density, mg./cm.²	23.3	31.6	32.6	35.7
Breaking strength wet (cut-strip), g.*	191	136	100	82
dry	227	215	183	151
Elongation, %* wet	48	50	63	69
dry	22	25	23	19
Tongue tear, work in in.-lb.*	3.11	2.55	1.95	1.51
Flexural rigidity, mg.-cm.†	127	169	253	609
Wrinkle recovery angle, degrees‡	149	146	138	131

ASTM, American Society for Testing Materials, Philadelphia, Pa. (*) D 39–49. (†) D 1388–55T. (‡) D 1295–53T.

The authors wish to thank Helen Kivela for technical assistance. They are also indebted to K. T. Williams and associates for analyses, Lura Brown for physical tests, F. T. Jones for birefringence values, and D. R. Black and K. J. Palmer for x-ray diffraction information.

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N. H. KOENIG
R. A. O'CONNELL

Book Review

Scientific Aspects of the Wool Industry. F. Monfort. Paris, Dunod, 1960. 514 pages. Price $17.50.

Reviewed by Werner von Bergen, J. P. Stevens & Co., Inc., Garfield, New Jersey

Since World War II textile research has a new aspect—the introduction of statistical methods which have multiple applications.

Although the field is still in progress, this book gathers results which are already proved and which are being constantly used by the author in industrial work. His function as secretary of the Technical Committee of the International Wool Federation has permitted him to observe attentively the reputable evolution of certain studies.

The introduction of these techniques manifested itself, as in other branches, by critical study of results obtained from tests (confidence, interval, etc.) and in the choice of the plan of execution of the experiences.

The fibers forming the fabric for a suit, these fibers being on a machine, constitute *a priori* masses on which can be applied probability and statistic reasoning. We are thus brought to consider the characteristics of a group of fabrics (fineness, length, etc.) as average parameter and distribution dispersion, that can be estimated from measurements of a sample. The behavior of the fibers in the machine can thus be better studied. Moreover, the desire to obtain regular threads leads one to imagine models of ideal threads, starting from a definite hypothesis. Thus the notion of regularity for a yarn appears under concrete aspects which are different and whose practical roles stand out more and more.

The majority of industrial questions may be examined by analysis of variants, the results of which make it possible to imagine a program aimed at reducing, if not completely eliminating, the annoying causes of fluctuation. The statistical control of operations sometimes results in diminishing their number (for example, the number of passages in the preparation).

Written in a very simple manner, complete with bibliographical references at the end of each chapter, this book will interest directly the engineers in the wool industry, but those of other textile branches can also be attracted, due to the general character of most chapters. Students of technical schools, in studying this book, will become acquainted with the scientific approach to the textile industry, which is now the trend.

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